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Evaluated kinetic and photochemical data for atmospheric chemistry: volume VIII – gas-phase reactions of organic species with four, or more, carbon atoms ($\geq C_4$)

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Detailed data sheets for the gas phase reactions of organic species with four, or more, carbon atoms ($\geq C_4$), IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (http://iupac.pole-ether.fr/), access date: January 25th 2021.

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HOx_VOC7: *n*-butane

Last evaluated: January 2008; Last change in preferred values: January 2008

$$HO + CH_3CH_2CH_2CH_3 \rightarrow H_2O + CH_2CH_2CH_2CH_3 \quad (1)$$
$$\rightarrow H_2O + CH_3CHCH_2CH_3 \quad (2)$$

$\Delta H°(1) = -72.4$ kJ·mol^{-1}

$\Delta H°(2) = -86.6$ kJ·mol^{-1}

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.41 \times 10^{-11} \exp[-(524 \pm 93)/T]$	298-495	Greiner, 1970	FP-KS
$(2.56 \pm 0.08) \times 10^{-12}$	298		
$(2.35 \pm 0.35) \times 10^{-12}$	298	Stuhl, 1973	FP-RF
$(4.22 \pm 0.17) \times 10^{-12}$	298	Gordon and Mulac, 1975	PR-RA
$(4.15 \pm 0.17) \times 10^{-12}$	381		
$(4.98 \pm 0.17) \times 10^{-12}$	416		
$1.76 \times 10^{-11} \exp[-(559 \pm 151)/T]$	298-420	Perry et al., 1976	FP-RF
$(2.72 \pm 0.27) \times 10^{-12}$	298		
$(2.67 \pm 0.22) \times 10^{-12}$	297 ± 2	Paraskevopoulos and Nip, 1980	FP-RA
$(2.3 \pm 0.3) \times 10^{-12}$	295	Schmidt et al., 1985	PLP-LIF
$2.34 \times 10^{-17} T^{1.95} \exp(134/T)$	294-509	Droege and Tully, 1986	PLP-LIF
$(2.42 \pm 0.10) \times 10^{-12}$	294		
$(2.25 \pm 0.10) \times 10^{-12}$	297 ± 2	Abbatt et al., 1990	DF-LIF
$(2.32 \pm 0.08) \times 10^{-12}$	~298	Schiffman et al., 1991	PLP-IR
$2.04 \times 10^{-17} T^2 \exp[(85 \pm 8)/T]$	231-378	Talukdar et al., 1994	PLP-LIF
$(2.459 \pm 0.018) \times 10^{-12}$	299		
$(2.43 \pm 0.07) \times 10^{-12}$	300	Donahue et al., 1998	DF-LIF
$(2.74 \pm 0.08) \times 10^{-12}$	325		
$(2.87 \pm 0.09) \times 10^{-12}$	340		
$(3.48 \pm 0.10) \times 10^{-12}$	375		
$(3.54 \pm 0.11) \times 10^{-12}$	390		
$(2.6 \pm 0.5) \times 10^{-12}$	300	Chuong and Stevens, 2002	DF-LIF
$(2.6 \pm 0.2) \times 10^{-12}$	300		
$(1.00 \pm 0.03) \times 10^{-12}$	185	Donahue and Clarke, 2004	DF-LIF (a)
$(1.14 \pm 0.04) \times 10^{-12}$	195		
$(1.21 \pm 0.08) \times 10^{-12}$	205		
$(1.36 \pm 0.04) \times 10^{-12}$	215		
$(1.45 \pm 0.04) \times 10^{-12}$	225		
$(1.64 \pm 0.13) \times 10^{-12}$	235		
$(1.77 \pm 0.08) \times 10^{-12}$	245		
$(1.74 \pm 0.05) \times 10^{-12}$	255		
$(1.95 \pm 0.06) \times 10^{-12}$	265		
$(2.07 \pm 0.07) \times 10^{-12}$	275		
$(2.17 \pm 0.06) \times 10^{-12}$	285		
$(2.54 \pm 0.08) \times 10^{-12}$	295		
Relative Rate Coefficients			
9.9×10^{-12}	753	Baker et al., 1970; Baldwin and Walker, 1979	RR (b)
$(9.3 \pm 0.8) \times 10^{-12}$	653	Hucknall et al, 1975	RR (c)
$(2.64 \pm 0.25) \times 10^{-12}$	299 ± 2	Atkinson et al., 1981	RR (d)
$(2.92 \pm 0.32) \times 10^{-12}$	295 ± 1	Atkinson and Aschmann, 1984	RR (d)

$(2.45 \pm 0.34) \times 10^{-12}$	300 ± 2	Barnes et al., 1986	RR (e)
$(2.36 \pm 0.04) \times 10^{-12}$	300	Behnke et al., 1988	RR (f)
$1.39 \times 10^{-11}\cdot\exp(-526/T)$	235-361	DeMore and Bayes, 1999	RR (g)
2.33×10^{-12}	298		
$(1.66 \pm 0.04) \times 10^{-12}$	248	Han et al., 2018	RR (h)
$(2.16 \pm 0.04) \times 10^{-12}$	288		

Comments

(a) Indicated errors are one standard deviation. Overall uncertainties were assessed to be ±7.5% for temperatures >250 K and ±10% for temperatures <250 K.

(b) Derived from the effects of the addition of small amounts of *n*-butane to slowly reacting mixtures of $H_2 + O_2$. The loss of H_2 was followed by monitoring the pressure change due to the reaction $2H_2 + O_2 \rightarrow 2H_2O$, and the loss of *n*-butane was measured by GC. The rate coefficient ratio *k*(HO + *n*-butane)/*k*(HO + H_2) = 13.2 is placed on an absolute basis using *k*(HO + H_2) = 7.87×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 753 K (Atkinson, 2003).

(c) HO radicals were generated by the decomposition of H_2O_2 in a boric acid-coated reaction vessel, and the concentrations of *n*-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios of *k*(HO + *n*-butane)/*k*(HO + propane) = 1.54 ± 0.13 is placed on an absolute value using *k*(HO + propane) = 6.16×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 653 K (IUPAC, 2019).

(d) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of *n*-butane and propene (the reference compound) were measured by GC. The measured rate coefficient ratios of *k*(HO + *n*-butane)/*k*(HO + propene) = 0.0962 ± 0.0093 at 299 ± 2 K (Atkinson et al., 1981) and 0.101 ± 0.012 at 295 ± 1 K (Atkinson and Aschmann, 1984) are placed on an absolute value using *k*(HO + propene) = 2.85×10^{-11} at 299 K and 2.89×10^{-11} at 295 K cm^3 $molecule^{-1}$ s^{-1} at atmospheric pressure of air (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of H_2O_2 in air at atmospheric pressure, and the concentrations of *n*-butane and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of *k*(HO + *n*-butane)/*k*(HO + ethene) = 0.32 ± 0.04 is placed on an absolute basis using *k*(HO + ethene) = 7.78×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 300 K and atmospheric pressure of air (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of NO_x-organic-air mixtures at atmospheric pressure. The concentrations of *n*-butane and *n*-octane (the reference compound) were measured by GC, and the measured rate coefficient ratio of *k*(HO + *n*-butane)/*k*(HO + *n*-octane) is placed on an absolute basis using *k*(HO + *n*-octane) = 8.15×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 300 K (Atkinson, 2003).

(g) HO radicals were generated by the photolysis of H_2O at 185 nm or, at low temperatures, by the photolysis of N_2O at 185 nm in the presence of H_2. The concentrations of *n*-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios *k*(HO + *n*-butane)/*k*(HO + propane) are placed on an absolute basis using a rate coefficient of *k*(HO + propane) = $1.65 \times 10^{-17}\ T^2 \exp(87/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

(h) The rate coefficient was measured at atmospheric pressure of purified air in a photochemical reactor (3.2 m^3 glass chamber) by the relative rate technique. HO radicals were generated by the photolysis of CH_3ONO at wavelengths > 300 nm. The concentrations of *n*-butane and the reference compounds (toluene and *n*-pentane) were measured by GC-FID. The measured rate coefficient ratios of *k*(HO + *n*-butane)/*k*(HO + toluene) and *k*(HO + *n*-butane)/*k*(HO + *n*-pentane) were not given by the authors, they were placed on an absolute basis using k(HO + toluene) = 7.09 × 10^{-12} at 248 K and 5.86 × 10^{-12} at 288 K and k(HO + n-pentane) = 2.93 × 10^{-12} at 248 K 3.62 × 10^{-12} at 288 K (in cm^3 $molecule^{-1}$ s^{-1}). The values in the table are the average of the data obtained relative to HO + toluene and HO + n-pentane.

Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	2.35 × 10^{-12}	298
k /cm^3 $molecule^{-1}$ s^{-1}	9.8 × 10^{-12} exp(-425/T)	180-300
Reliability		
Δ log k	± 0.06	298
Δ E/R	± 100	180-300

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients of Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1998) and Donahue and Clarke (2004) and the relative rate coefficients of DeMore and Bayes (1999). An Arrhenius plot of the rate coefficients from these studies (Droege and Tully, 1986; Abbatt et al., 1990; Talukdar et al., 1994; Donahue et al., 1998; DeMore and Bayes, 1999; Donahue and Clarke, 2004) plus the higher temperature relative rate data of Baker et al. (1970) [as re-evaluated by Baldwin and Walker (1979)] and Hucknall et al. (1975), is clearly curved (see Arrhenius plot).

The rate coefficients from the studies of Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1998), DeMore and Bayes (1999) and Donahue and Clarke (2004) are fitted using the three parameter expression, $k = CT^2 \exp(-D/T)$, resulting in $k = 2.03 \times 10^{-17}\, T^2 \exp(78/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 185-509 K. This expression also fits the higher temperature rate coefficient of Hucknall et al. (1975) extremely well. An Arrhenius fit, $k = A \exp(-B/T)$, of the rate coefficients from Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994), Donahue et al. (1998), DeMore and Bayes (1999) and Donahue and Clarke (2004) at temperatures ≤300 K results in $k = 9.82 \times 10^{-12} \exp(-427/T)$ cm^3 $molecule^{-1}$ s^{-1}. As shown in the Arrhenius plot, this is an excellent representation of the rate coefficients from these studies at ≤ 300 K, and is the recommended Arrhenius expression. The preferred values are in good agreement with the room temperature absolute and relative rate coefficients of Greiner (1970), Stuhl (1973), Perry et al. (1976), Paraskevopoulos and Nip (1980), Schmidt et al. (1985), Schiffman et al. (1991), Atkinson et al. (1981), Atkinson and Aschmann (1984), Barnes et al. (1986), Behnke et al. (1988) and Chuong and Stevens (2002) which were not used in the evaluation of the rate coefficient.

Note that the Arrhenius expression derived from the 3-parameter fit, centered at 225 K with $A = C e^2 T^2$ and $B = D + 2T$, of $k = 7.59 \times 10^{-12} \exp(-372/T)$ cm^3 $molecule^{-1}$ s^{-1} results in predicted rate coefficients 8% lower at 300 K and 5% higher at 180 K than those calculated from the preferred Arrhenius fit of the rate coefficients at ≤ 300 K.

Droege and Tully (1986) also measured rate coefficients for the reaction of the HO radical with n-butane-d_{10}, and derived a value of $k_1/k_2 = 1.035 \exp(-536/T)$, leading to $k_1 = 3.4 \times 10^{-13}$ at 298 K and $k_2 = 2.00 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K. k_1 and k_2 being the rate coefficients for the D-atom abstraction from CD_3- and –CD_2- groups, respectively.

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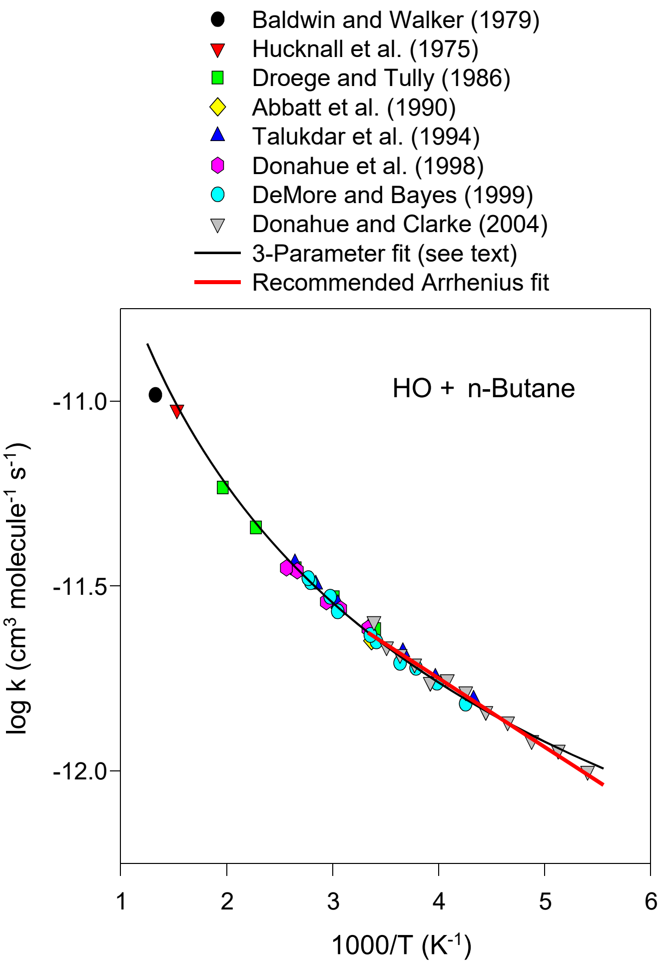


Rate coefficients for HO + *n*-butane.

HOx_VOC8: isoprene

Last evaluated: December 2019; Last change in preferred values: December 2019

HO + $CH_2=C(CH_3)CH=CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.36 \times 10^{-11} \exp[(409 \pm 28)/T]$	299-422	Kleindienst et al., 1982	FP-RF
$(9.26 \pm 1.5) \times 10^{-11}$	299		
$9.7 \times 10^{-11} (T/298)^{-1.36}$	249-348	Siese et al., 1994	FP-RF
9.7×10^{-11}	298		
$(1.10 \pm 0.05) \times 10^{-10}$	298	Stevens et al., 1999	DF-LIF
$2.70 \times 10^{-11} \exp[(336 \pm 74)/T]$	251-342	Campuzano-Jost et al., 2000	PLP-LIF (a)
$(8.56 \pm 0.26) \times 10^{-11}$	297		
$(1.10 \pm 0.04) \times 10^{-10}$	300	Chuong and Stevens, 2000	DF-LIF (b)
$(9.6 \pm 0.5) \times 10^{-11}$	295	McGivern et al., 2000	PLP-LIF (c)
$(1.01 \pm 0.08) \times 10^{-10}$	298 ± 2	Zhang et al., 2000	DF-CIMS (d)
9.1×10^{-11}	298 ± 2	Zhang et al., 2001	DF-CIMS (e)
$(1.08 \pm 0.05) \times 10^{-10}$	300	Chuong and Stevens, 2002	DF-LIF (f)
$2.68 \times 10^{-11} \exp[(348 \pm 136)/T]$	251-342	Campuzano-Jost et al., 2004	PLP-LIF (g)
$(8.47 \pm 0.59) \times 10^{-11}$	297		
$(1.00 \pm 0.15) \times 10^{-10}$	293	Spangenberg et al., 2004	PLP-LIF (h)
$(1.00 \pm 0.12) \times 10^{-10}$	294 ± 1.1	Karl et al., 2004	(i)
$(1.02 \pm 0.09) \times 10^{-10}$	295 ± 1	Poppe et al., 2007	(i)
$(1.12 \pm 0.07) \times 10^{-10}$	296 ± 2		
$(1.07 \pm 0.08) \times 10^{-10}$	290.5 ± 2.5		
$(9.7 \pm 0.8) \times 10^{-11}$	291 ± 2		
$(9.9 \pm 0.8) \times 10^{-11}$	290 ± 1		
$1.93 \times 10^{-11} \exp[(466 \pm 12)/T]$	241-356	Dillon et al., 2017	PLP-LIF (j)
$(9.3 \pm 0.4) \times 10^{-11}$	297		
$1.80 \times 10^{-11} \exp[(522 \pm 28)/T]$	298-794	Medeiros et al., 2018	PLP-LIF (k),(l)
$(9.90 \pm 0.09) \times 10^{-11}$	298		(k),(l)
$(1.06 \pm 0.02) \times 10^{-10}$	298		(k),(m)
$(1.04 \pm 0.02) \times 10^{-10}$	298		(k),(n)
Relative Rate Coefficients			
7.2×10^{-11}	300	Cox et al., 1980	RR (o)
$(1.08 \pm 0.05) \times 10^{-10}$	299 ± 2	Atkinson et al., 1982	RR (p)
$(9.90 \pm 0.27) \times 10^{-11}$	297 ± 2	Ohta, 1983	RR (q)
$(1.10 \pm 0.04) \times 10^{-10}$	295 ± 1	Atkinson and Aschmann, 1984	RR (r)
$(1.09 \pm 0.02) \times 10^{-10}$	297 ± 1	Edney et al., 1986	RR (s)
$(1.11 \pm 0.23) \times 10^{-10}$	298	McQuaid et al., 2002	RR (t)
$2.54 \times 10^{-11} \exp[(409 \pm 42)/T]$	298-363	Gill and Hites, 2002	RR (u)
$(1.00 \pm 0.05) \times 10^{-10}$	298		
$(1.06 \pm 0.04) \times 10^{-10}$	298 ± 2	Iida et al., 2002	RR (v)
$2.33 \times 10^{-11} \exp[(444 \pm 27)/T]$	240-340	Singh and Li, 2007	RR (w)
$(1.07 \pm 0.03) \times 10^{-10}$	298		RR (w,x)
$(1.11 \pm 0.02) \times 10^{-10}$	298		RR (w,y)
$3.97 \times 10^{-11} \exp[(249 \pm 20)/T]$	323-413	Hites and Turner, 2009	RR (u)

Comments

(a) Rate coefficients for the reactions of HO radicals with isoprene-d_6 and DO radicals with isoprene were also measured at 297 K, these being $(8.31 \pm 0.10) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(8.27 \pm 0.10) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively.

(b) Carried out at total pressures of 2-6 Torr (2.7-8.0 mbar) of helium diluent. No pressure dependence of the rate coefficient was observed at 300 K. However, at higher temperatures (321-423 K) the rate coefficient increased with increasing total pressure, with the effect being more pronounced at higher temperature.

(c) Carried out at total pressures of 0.5-20 Torr (0.7-27 mbar) of argon diluent. The rate coefficient was observed to be pressure dependent below 10 Torr total pressure; the value cited in the table is that measured at 20 Torr total pressure.

(d) Carried out at total pressures of 72.7-112.7 Torr (97-150 mbar) of N_2 diluent. The measured rate coefficient was independent of pressure over this range.

(e) Based on a very limited kinetic study carried out at a total pressure of 1.9 Torr (2.5 mbar) of helium diluent (the focus of the study was on formation of HO-isoprene adducts and their subsequent reactions).

(f) Carried out at total pressures of argon diluent of 100 Torr (133 mbar) and 150 Torr (200 mbar). The measured rate coefficient was independent of total pressure over this range.

(g) Rate coefficients for HO + isoprene-d_6 and DO + isoprene were also measured at 297 K, with values of $(8.27 \pm 0.17) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $(8.43 \pm 0.18) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. Isoprene and isoprene-d_6 concentrations in the gas flow stream were measured before and after the reaction cell by UV absorption at 228.9 nm. The data from this study are in excellent agreement with those previously reported by Campuzano-Jost et al. (2000) at the same temperatures, and are assumed to supersede the earlier study.

(h) Rate coefficients were also measured at 58, 71, 84, 104 and 114 K, with the rate coefficients of $(7.8 \pm 1.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $(1.14 \pm 0.17) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, $(9.8 \pm 1.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, $(1.88 \pm 0.28) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $(1.68 \pm 0.25) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively.

(i) Carried out in a large volume (270 m^3) chamber. HO radicals were measured by LIF and isoprene was measured by GC (Karl et al., 2004; Poppe et al., 2007) or by proton-transfer-reaction mass spectrometry (Poppe et al., 2007) during irradiations of air mixtures containing low concentrations of isoprene and NO_x.

(j) Pulsed laser photolysis of H_2O_2 at 248 nm, in the presence of isoprene/N_2 or isoprene/air mixtures at total pressures in the range 3.8-165 Torr (5.1-220 mbar). Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of isoprene (monitored by vacuum UV optical absorption at 184.95 nm). k displayed no significant dependence on bath gas or on pressure over the studied range (N.B. The room temperature, 296-298 K, data points presented below were obtained at 3.8, 7.5, 42.9, 71.0, 103 and 165 Torr in N_2 and at 103 and 165 Torr in air. The reported value, tabulated above, is based on the average of the six N_2 determinations).

(k) Pulsed laser photolysis of H_2O_2 or t-C_4H_9OOH at 248 nm, in the presence of isoprene/N_2 or isoprene/N_2/O_2 mixtures. Experiments carried out in either a high pressure apparatus, at total pressures of 1290-1670 Torr (1720-2230 mbar), or in a low pressure apparatus, at total pressures of 50-140 Torr (66-187 mbar). Decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of isoprene. k displayed no significant dependence pressure or HO radical source, and the tabulated temperature dependence expression is based on the combined dataset, also reported as $k = (10.4 \pm 0.4) \times 10^{-11} (T/298)^{-1.34\pm0.12}$. Evidence for H atom abstraction observed from [HO] decays at T > 700 K, when the reversible HO addition routes are equilibrated. Based on support from theoretical calculations, and from PTR-TOF-MS measurements of product formation at $m/z = 83$ (attributed to 2-methylene-but-3-enal following abstraction from CH_3 group in the presence of O_2) at 298-473 K, the following expressions were also recommended for high-pressure limiting HO addition (k_{add}) and H abstraction (k_{abs}): $k_{add} = (9.5 \pm 0.2) \times 10^{-11} (T/298)^{-1.33\pm0.07}$; $k_{abs} = (1.3 \pm 0.3) \times 10^{-11} \exp(-3.61 \text{kJmol}^{-1}/RT)$; where $k = k_{add} + k_{abs}$.

(l) k determined from high pressure measurements. HO generated by H_2O_2 photolysis.

(m) k determined from low pressure measurements. HO generated by H_2O_2 photolysis.

(n) k determined from low pressure measurements. HO generated by t-C_4H_9OOH photolysis.

(o) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of HONO at wavelengths >300 nm. The concentrations of isoprene and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + isoprene)/k(HO + ethene) is placed on an absolute basis by use of a rate coefficient of k(HO + ethene) = 7.78×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 300 K and atmospheric pressure of air (IUPAC, 2019).

(p) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths >300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + propene) = 3.81 ± 0.17 is placed on an absolute basis by use of a rate coefficient of k(HO + propene) = 2.85×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 299 K and atmospheric pressure of air (IUPAC, 2019).

(q) Relative rate method carried out at atmospheric pressure of $N_2 + O_2$. HO radicals were generated by photolysis of H_2O_2 at 253.7 nm. The concentrations of isoprene and 1,3-butadiene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + 1,3-butadiene) = 1.48 ± 0.04 is placed on an absolute basis by use of a rate coefficient of k(HO + 1,3-butadiene) = 6.69×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 297 K and atmospheric pressure of air (Atkinson and Arey, 2003).

(r) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths >300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + propene) = 3.81 ± 0.15 is placed on an absolute basis by use of a rate coefficient of k(HO + propene) = 2.89×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 295 K and atmospheric pressure of air (IUPAC, 2019).

(s) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths >300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + propene) is placed on an absolute basis by use of a rate coefficient of k(HO + propene) = 2.87×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 297 K and atmospheric pressure of air (IUPAC, 2019).

(t) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + isoprene)/k(HO + *trans*-butene) = 1.74 ± 0.14 is placed on an absolute basis by use of a rate coefficient of k(HO + *trans*-2-butene) = 6.40×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K and atmospheric pressure of air (IUPAC, 2019). The cited error limits are the 95% confidence intervals (McQuaid et al., 2002).

(u) Relative rate method carried out in a 192 cm^3 volume quartz reaction vessel at atmospheric pressure of helium diluent. HO radicals were generated by photolysis of H_2O_2. The concentrations of isoprene and 2-methylpropene (the reference compound) were measured by MS. Rate coefficients were measured over the temperature ranges 298-363 K by Gill and Hites (2002) and 323-413 K by Hites and Turner (2009). The measured rate coefficient ratios of k(HO + isoprene)/k(HO + 2-methylpropene) are placed on an absolute basis by use of a rate coefficient of k(HO + 2-methylpropene) = $9.4 \times 10^{-12} \exp(505/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019). The cited Arrhenius expression for the Hites and Turner (2009) study is an un-weighted least-squares fit to their data; the cited error in the temperature dependence is two standard deviations. Combination of the rate coefficients of Gill and Hites (2002) and Hites and Turner (2009) results in the Arrhenius expression $k = 3.12 \times 10^{-11} \exp[(339 \pm 19)/T]$ cm^3 molecule^{-1} s^{-1} or, because the combined data suggested a curved Arrhenius plot, $k = 3.44 \times 10^{-17}\, T^2 \exp[(1037 \pm 14)/T]$ cm^3 molecule^{-1} s^{-1} (Hites and Turner, 2009), both relative to k(HO + 2-methylpropene) = $9.4 \times 10^{-12} \exp(505/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(v) Carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO. The concentrations of isoprene and cyclohexane, di-*n*-butyl ether or propene (the reference compounds) were measured by FTIR spectroscopy. The measured rate coefficient ratios of k(HO + isoprene)/k(HO + cyclohexane) = 14.3 ± 1.2 and 1.49 ± 1.3, k(HO + isoprene)/k(HO + di-*n*-butyl ether) = 3.71 ± 0.14 and 3.61 ± 0.23, and k(HO + isoprene)/k(HO + propene) = 3.89 ± 0.20, 3.96 ± 0.18, 3.90 ± 0.15 and 3.98 ± 0.20 are placed on an absolute basis by use of rate coefficients at 298 K and atmospheric pressure of air of k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003), k(HO + di-*n*-butyl ether) = 2.78×10^{-11} cm^3 molecule^{-1} s^{-1} (Mellouki et al., 1995) and k(HO + propene) = 2.86×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019). The value in the table is the un-weighted average together with the two standard deviation error.

(w) Discharge flow system with MS detection of isoprene and the reference compounds dimethyl disulfide and ethanethiol. HO radicals generated by the reaction F + H_2O. Total pressure was in the range 1-3 Torr (1.3-4 mbar). The rate coefficient for the HO + isoprene reaction was independent of pressure over the range 1-3 Torr at 298 K, but was increased with increasing pressure over the range 1-3 Torr at 340 K. Temperature-dependent rate measurements were carried out at 1.0-1.1 Torr pressure, and hence the rate coefficient at 340 K would have been in the fall-off region. The measured rate coefficient ratios (which were tabulated only at 298 K) were placed on an absolute basis using k(HO + dimethyl disulfide) = $5.9 \times 10^{-11} \exp(380/T)$ cm^3 molecule^{-1} s^{-1} (Wine et al., 1981) and k(HO + ethanethiol) = $1.23 \times 10^{-11} \exp(396/T)$ cm^3 molecule^{-1} s^{-1} (Wine et al., 1984). The rate coefficient used for k(HO + dimethyl disulfide) is slightly different from the IUPAC recommendation of $7.0 \times 10^{-11} \exp(350/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019), but re-evaluation is only possible for the 298 K rate coefficient (see Comment (x) below).

(x) Relative to dimethyl disulfide. The measured rate coefficient ratio k(HO + isoprene)/k(HO + dimethyl disulfide) = 0.464 ± 0.010 at 298 K is placed on an absolute basis using k(HO + dimethyl disulfide) = 2.3×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(y) Relative to ethanethiol. The measured rate coefficient ratio k(HO + isoprene)/k(HO + ethanethiol) = 2.398 ± 0.043 at 298 K is placed on an absolute basis using k(HO + ethanethiol) = 4.64×10^{-11} cm^3 molecule^{-1} s^{-1} (Wine et al., 1984).

Preferred Values

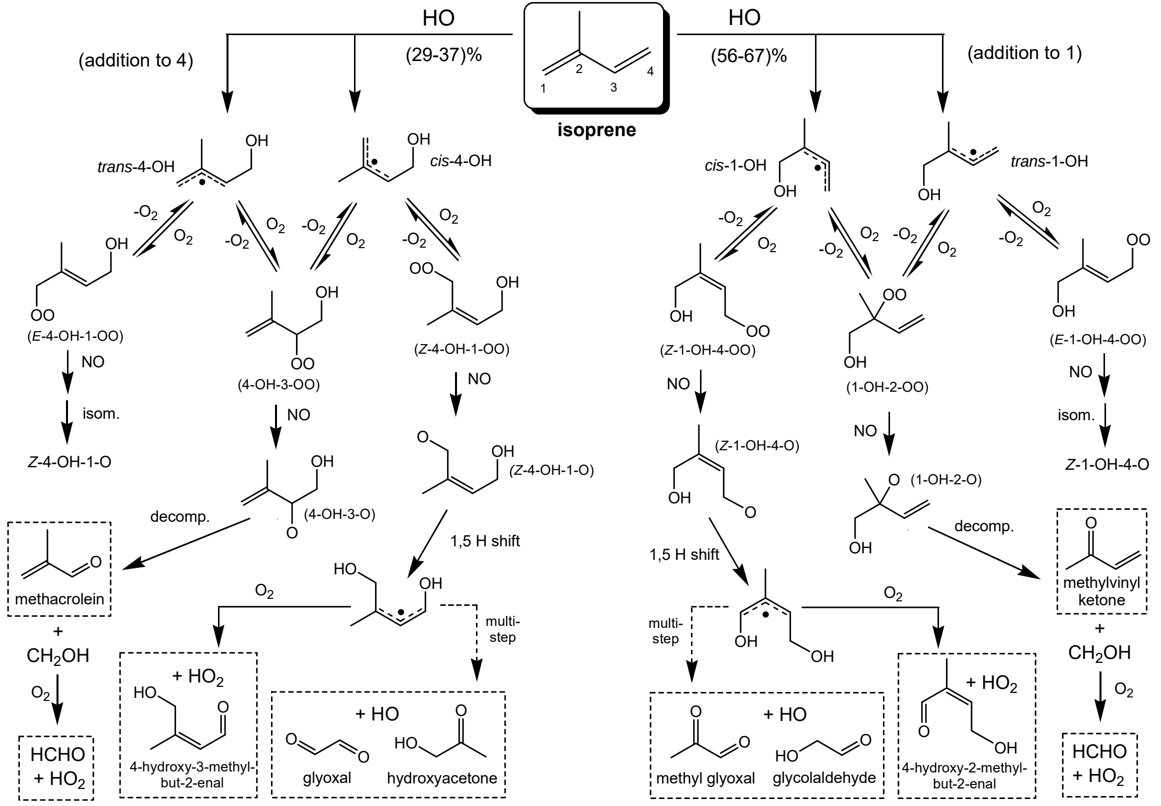
Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-10}	298
k /cm^3 molecule^{-1} s^{-1}	2.10×10^{-11} exp(465/T)	240-630
Reliability		
$\Delta \log k$	± 0.06	298
$\Delta E/R$	± 150	

Comments on Preferred Values

The reaction of HO radicals with isoprene has been studied extensively, and the room temperature values of k in the reported absolute and relative rate studies are generally in very good agreement. The preferred value of E/R is the average of those reported in the direct studies of Kleindienst et al. (1982), Dillon et al. (2017) and Medeiros et al. (2018), which collectively cover the complete temperature range of the recommendation. The slightly lower values of E/R reported in the direct studies of Siese et al. (1994) and Campuzano-Jost et al. (2000; 2004), and those in the relative rate studies of Gill and Hites (2002) and Singh and Li (2007) also lie within the assigned uncertainty bounds. The 298 K preferred value of k is an average of the room temperature values reported in the direct studies of Kleindienst et al. (1982), Siese et al. (1994), Stevens et al. (1999), Chuong and Stevens (2000; 2002), McGivern et al. (2000), Zhang et al. (2000; 2001), Karl et al. (2004)/Poppe et al. (2007), Dillon et al. (2017) and Medeiros et al. (2018), corrected to 298 K where necessary using the preferred temperature dependence. For each of the related pairs of studies, Chuong and Stevens (2000; 2002), Zhang et al. (2000; 2001) and Karl et al. (2004)/Poppe et al. (2007), a single unweighted average was applied in the above procedure. The rate coefficients reported by Campuzano-Jost et al. (2000; 2004) and Cox et al. (1980) are about 15 % and 27 % lower than the preferred value.

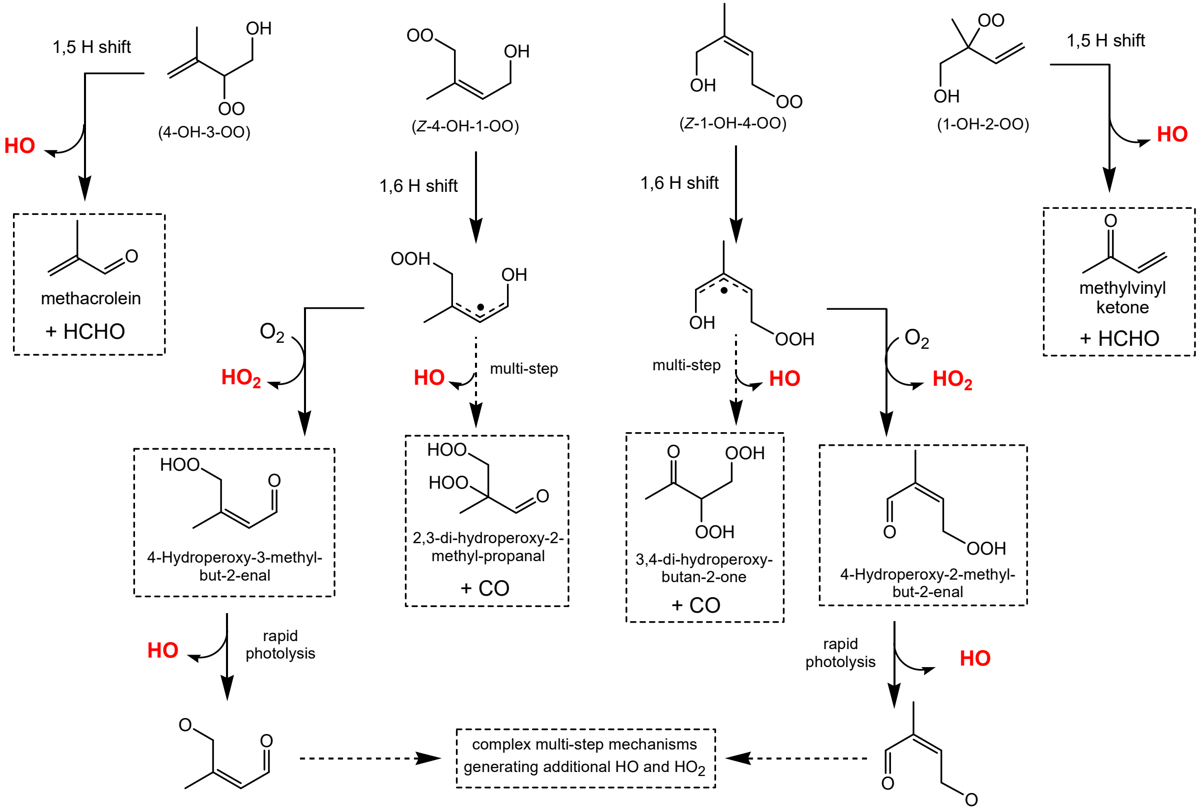
On the basis of theoretical studies (e.g. Vereecken and Peeters, 2001) and structure-activity relationship (SAR) methods (e.g. Jenkin et al., 2018), H atom abstraction has generally been estimated to account for only a very minor fraction (~0.3 %) of the reaction of HO with isoprene at 298 K and 1 bar pressure, with this occurring from the -CH_3 group. This is expected to increase at higher temperatures, and strong evidence for H atom abstraction at $T > 700$ K has been reported by Medeiros et al. (2018) (see comment (k)). They also tentatively suggested that H atom abstraction may account for as much as (3 ± 2) % of the reaction at 298 K, with support from PTR-TOF-MS measurements of product formation at $m/z = 83$, attributed to 2-methylene-but-3-enal. However, this observation may be complicated by formation of the isobaric species, 3-methylfuran, a reported minor product of the HO + isoprene reaction (see below).

The reaction thus proceeds almost exclusively by initial addition of HO to the C=C bonds. Theoretical calculations and SAR methods predict that the percentages of HO radical addition to the 1-, 2-, 3- and 4-position carbon atoms at 298 K lie in the ranges (56–67) %, (2–4) %, (2–5) % and (29–37)%, respectively (e.g. McGivern et al., 2000; Lei et al., 2000; Greenwald et al., 2007; Peeters et al., 2014; Jenkin et al., 2018), with these percentages being relatively insensitive to changes in temperature and pressure over the atmospheric ranges (Greenwald et al., 2007). Addition to the terminal carbon atoms therefore dominates, with subsequent (reversible) addition of O_2 leading to the formation of the six hydroxyallyl peroxy radicals shown in the schematic below (Peeters et al., 2009), with the species nomenclature also based on that study.



The subsequent chemistry has been reviewed in detail by Jenkin et al. (2015) and Wennberg et al. (2018). The majority of reported product studies have traditionally been carried out at atmospheric pressure in the presence of sufficient NO (> 500 ppb), so that the hydroxyallyl peroxy radicals react predominantly with NO at a rate that is much faster than their back decomposition rates. Under these conditions, the chemistry propagated by the reactions with NO forms a number of carbonyl and hydroxycarbonyl end products (shown in boxes), with the following molar yields, e.g. see Jenkin et al. (2015) and Wennberg et al. (2018), and references therein: methyl vinyl ketone, (32–44%), methacrolein (22–28%), formaldehyde (57–66%), 4-hydroxy-2-methyl-but-2-enal and 4-hydroxy-3-methyl-but-2-enal (10–20%), glyoxal (2.1–3%), glycolaldehyde (2.7–4.2%) and hydroxyacetone (2.9–3.8%). Minor formation (≤ 5%) of 3-methylfuran has also been reported (not shown in the schematic). This may be formed from isomerisation and dehydration of the product oxy radicals, Z-1-OH-4-O and Z-4-OH-1-O (Francisco-Márquez et al., 2003), but is also likely formed from secondary cyclisation and dehydration of 4-hydroxy-2-methyl-but-2-enal and 4-hydroxy-3-methyl-but-2-enal, possibly heterogeneously (Dibble, 2007). The reactions of the hydroxyallyl peroxy radicals with NO also partially form the corresponding hydroxy-nitrate products (not shown in the schematic), which have been reported to be formed with a collective yield of 4-15% (see data sheet ROO_50).

Other reactions of the hydroxyallyl peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low NO_x levels. These include bimolecular reactions with HO_2 and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products (Ruppert and Becker, 2000; Benkelberg et al., 2000; Lee et al., 2005). However, a major advance in understanding in recent years has been the recognition of an important role for unimolecular isomerisation reactions of some of the hydroxyallyl peroxy radical isomers (e.g. Peeters et al., 2009; 2014), namely 1,5 H shift reactions for 1-OH-2-OO and 4-OH-3-OO and, more significantly, 1,6 H shift reactions *Z*-1-OH-4-OO and *Z*-4-OH-1-OO, as shown below.



These reactions, in conjunction with interconversion of the hydroxyallyl peroxy radical isomers (*via* the reversible O_2 + OH-isoprene adduct reactions discussed above), provide significant routes for regeneration of HO_x radicals under the low NO_x conditions of the remote atmospheric boundary layer. Usually referred to as the Leuven Isoprene Mechanism (LIM), this subset of the chemistry was originally proposed and characterised in the theoretical studies of Peeters et al. (2009; 2014). It has been largely verified by laboratory experimental studies (Wennberg et al., 2018), and this mechanism and related chemistry continues to be a focus of ongoing experimental and theoretical studies.

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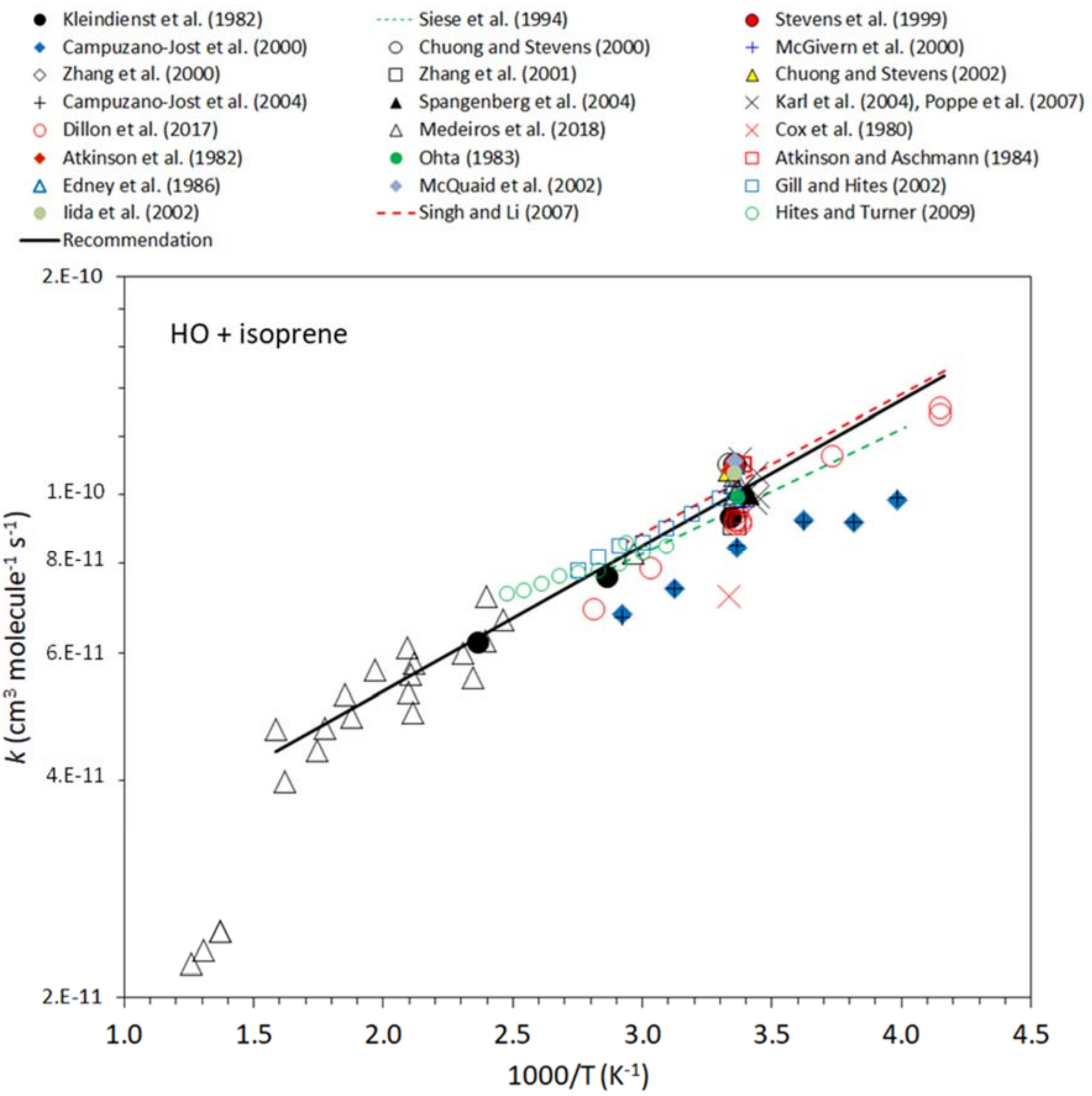
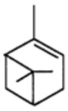


Rate coefficients for HO + isoprene.

HOx_VOC9: α-pinene

Last evaluated: December 2017; Last change in preferred values: June 2019

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.37 \times 10^{-11} \exp[(446 \pm 76)/T]$	298-422	Kleindienst et al., 1982	FP-RF (a)
$(6.01 \pm 0.82) \times 10^{-11}$	298		
$1.63 \times 10^{-12} \exp[(1080 \pm 50)/T]$	300-435	Chuong et al., 2002	DF-RF/LIF (b)
$(6.08 \pm 0.24) \times 10^{-11}$	300		
$(6.09 \pm 0.30) \times 10^{-11}$	300	Davis and Stevens, 2005	DF-LIF (c)
$1.83 \times 10^{-11} \exp[(330 \pm 6)/T]$	238-357	Dillon et al., 2017	PLP-LIF (d)
$(5.4 \pm 0.2) \times 10^{-11}$	296		
Relative Rate Coefficients			
$(5.6 \pm 1.7) \times 10^{-11}$	305 ± 2	Winer et al., 1976	RR/P-GC-FID (e)
$(5.36 \pm 0.31) \times 10^{-11}$	294 ± 1	Atkinson et al., 1986	RR/P-GC-FID (f)
$1.17 \times 10^{-11} \exp[(436 \pm 53)/T]$	295-364	Gill and Hites, 2002	RR/P-MS (g)
$(5.04 \pm 1.23) \times 10^{-11}$	298		
$1.40 \times 10^{-11} \exp[(387 \pm 46)/T]$	240-340	Montenegro et al., 2012	RR/DF-MS (h)
$(5.36 \pm 0.94) \times 10^{-11}$	298		
$(5.06 \pm 0.75) \times 10^{-11}$	298	Dash et al. 2014	RR/P-GC-FID (i)

α-pinene is 2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene

Comments

(a) Flash photolysis of H_2O/α-pinene mixtures in Ar (buffer gas) at total pressures in the range 50-200 Torr (67-270 mbar) under slow flow conditions. Pseudo-first order decays of HO radical concentrations (monitored by RF) were characterized in the presence of excess concentrations of α-pinene. k displayed no dependence on pressure over the studied range.

(b) Pseudo-first order decays of HO radical concentrations (monitored by RF or LIF) were characterized in the presence of excess concentrations of α-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of either He or 90% He and 10% O_2.

(c) Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of α-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of mainly He, with O_2 present at ~ 1-14% of the mixture.

(d) Pulsed laser photolysis of H_2O_2 at 248 nm, in the presence of α-pinene/N_2 or α-pinene/air mixtures at total pressures in the range 6-211 Torr (8-280 mbar). Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of α-pinene (monitored by vacuum UV optical absorption at 184.95 nm). k displayed no significant dependence on bath gas or on pressure over the studied range (N.B. The 296 K data points presented below were obtained at 7.5, 96 and 197 Torr in N_2 and at 97 Torr in air. The reported value, tabulated above, is based on the average of the four determinations).

(e) HO radicals were generated by the photolysis of NO_x – organic – air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of α-pinene and 2-methylpropene (the reference compound) were analyzed by GC. The measured rate coefficient ratio k(HO + α-pinene)/k(HO + 2-methylpropene) = 1.14 (± 30%) is placed on an absolute basis using k(HO + 2-methylpropene) = 4.92×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 305 K (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of α-pinene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during the CH_3ONO – NO - α-pinene - 2,3-dimethyl-2-butene – air irradiations. The measured rate coefficient ratio k(HO + α-pinene)/k(HO + 2,3-dimethyl-2-butene) = 0.487 ± 0.028 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.10×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(g) HO radicals were generated by the photolysis of H_2O_2 in helium diluent in a 192 cm^3 volume quartz vessel. The concentrations of α-pinene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS during the experiments. The measured rate coefficient ratios k(HO + α-pinene)/k(HO + 1-butene), k(HO + α-pinene)/k(HO + 2-methylpropene) and k(HO + α-pinene)/k(HO + *trans*-2-butene) are placed on an absolute basis using k(HO + 1-butene) = $6.6 \times 10^{-12} \exp(465/T)$ cm^3 $molecule^{-1}$ s^{-1}, k(HO + 2-methylpropene) = $9.4 \times 10^{-12} \exp(505/T)$ cm^3 $molecule^{-1}$ s^{-1} and k(HO + *trans*-2-butene) = $1.0 \times 10^{-11} \exp(553/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

(h) HO radicals were generated by the reaction of H_2O with F atoms (formed from F_2 discharge), and added to flowing mixtures containing α-pinene and isoprene (the reference compound) in helium at a total pressure of 1-8 Torr (1.3-11 mbar). The measured rate coefficient ratios, k(HO + α-pinene)/k(HO + isoprene), are placed on an absolute basis using the rate coefficient expression k(HO + isoprene) = $2.7 \times 10^{-11} \exp(370/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

(i) HO radicals were generated by the photolysis of H_2O_2 in nitrogen diluent at pressures in the range 800-850 Torr (1070-1130 mbar) in a 1750 cm^3 volume quartz vessel. The concentrations of α-pinene and propene (the reference compound) were analyzed by GC-FID. The measured rate coefficient ratio k(HO + α-pinene)/k(HO + propene) is placed on an absolute basis using k(HO + propene) = 2.86×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K and 825 Torr (1100 mbar) (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	5.3×10^{-11}	298
k /cm^3 $molecule^{-1}$ s^{-1}	$1.34 \times 10^{-11} \exp(410/T)$	240-360
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 100	240-360

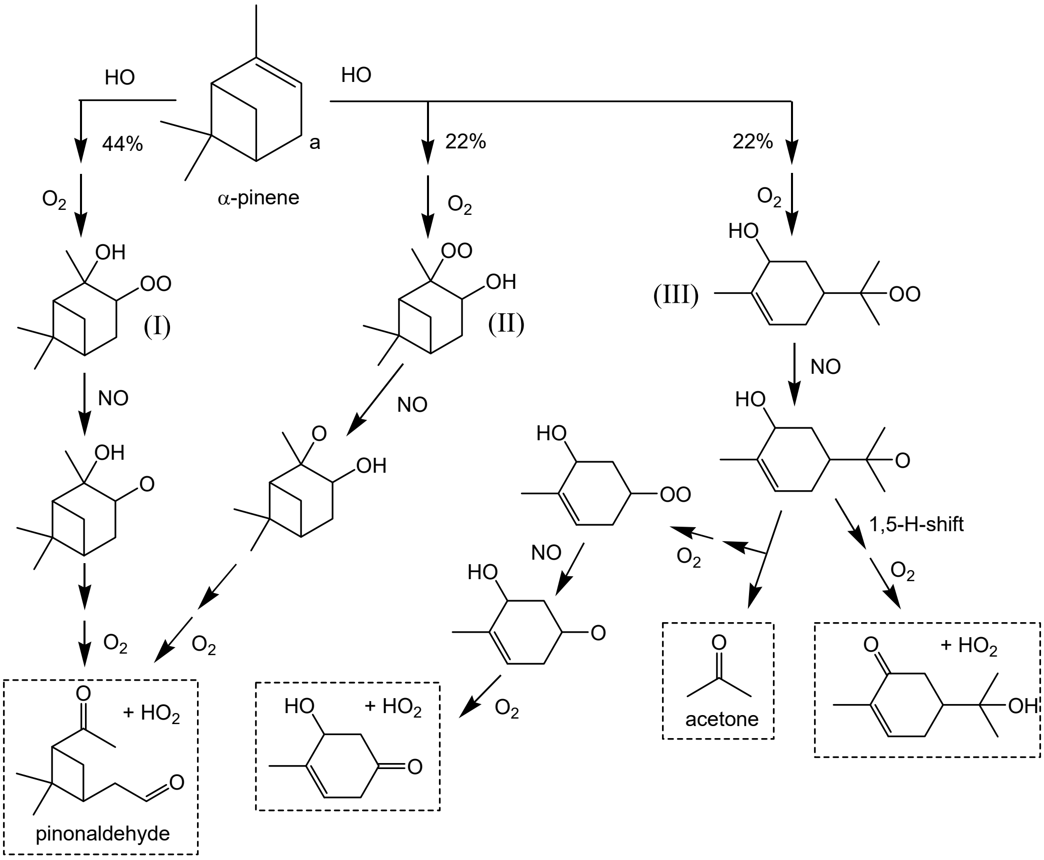
Comments on Preferred Values

The room temperature values of k in the reported studies are in reasonable agreement. With the exception of the recent study of Dillon et al. (2017), those reported in the direct kinetics studies are consistently slightly higher (15% on average) than those reported in the relative rate studies. The direct studies of Chuong et al. (2002) and Davis and Stevens (2005) reported increased wall removal rates of HO when α-pinene was present, and initial deviations from pseudo-first order

HO decay, which may contribute to the small systematic difference. Chuong et al. (2002) also report a temperature dependence that is significantly higher than those reported in other temperature dependence studies. Similar complications were not apparent in the recent direct study of Dillon et al. (2017), which reports a room temperature value of *k* that is comparable with those in the relative rate studies.

The preferred value of E/R is a rounded average of those reported in the relative rate studies of Gill and Hites (2002) and Montenegro et al. (2012), but is consistent with those reported in the direct studies of Kleindienst et al. (1982) and Dillon et al. (2017). The 298 K preferred value of *k* is an average of the room temperature values reported in all the tabulated relative rate studies, with those of Winer et al. (1976) and Atkinson et al. (1986) corrected to 298 K using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value. However, the resultant expression also provides an excellent description of the recent direct kinetics data of Dillon et al. (2017) at temperatures below 300 K.

H atom abstraction has been estimated to account for about 12 % of the reaction of HO with α-pinene at 298 K (Peeters et al., 2001); with this being dominated by attack at position “a” in the schematic below, which forms a resonant radical. The reaction proceeds mainly by initial addition of the HO radical to the C=C bond, and the schematic illustrates some features of the established and predicted subsequent chemistry in air in the presence of NO_x.



The hydroxy-substituted peroxy radicals, (I), (II) and (III), are formed from sequential addition of HO and O_2, with (III) facilitated by competitive opening of the cyclobutyl ring in the intermediate chemically-activated HO-α-pinene adduct. The approximate contributions of the three pathways shown are based on the calculations of Vereecken and Peeters (2000) and Peeters et al. (2001) for 298 K and 1 bar. The subsequent chemistry, propagated by the reactions of intermediate peroxy radicals with NO, forms a number of carbonyl end products (as shown in boxes). The chemistry of (I) and (II) generates pinonaldehyde, which has been reported to be formed in yields in the range 28 ± 5% to 87 ± 20% in experimental studies in the presence of NO_x (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1994; Nozière et al., 1999; Wisthaler et al., 2001; Aschmann et al., 2002). Lower yields have generally been obtained by GC analyses (Arey et al., 1990; Hakola et al., 1994; Aschmann et al., 2002) and by proton-transfer mass spectrometry (Wisthaler et al., 2001), with the higher values by *in situ* FTIR spectroscopy (Hatakeyama et al., 1991; Nozière et al., 1999). The chemistry of (III) partially generates acetone, which has been reported to be formed in yields in the range 5-11% (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000).

The reactions of all the peroxy radicals with NO also partially form the corresponding hydroxy-nitrate products (not shown in the schematic). There is some disagreement in the reported yields of nitrate products, with the *in situ* FTIR determinations of total nitrate products by Nozière et al. (1999), 18 ± 9%, and Rindelaub et al. (2015), 26 ± 7%, being much higher than those reported specifically for the C_{10} hydroxynitrates by Aschmann et al. (2002), ~ 1 %, and Xu et al. (2019), 3.3 ± 1.5%, based on mass spectrometric methods (API-MS and GC−ToF-CIMS, respectively). Other products have also been observed, including formaldehyde (19%) and formic acid (7%) by Orlando et al. (2000); and product signals consistent with a number of higher molecular weight dihydroxycarbonyl, hydroxynitrate and dihydroxynitrate products by Aschmann et al. (1998; 2002).

Other reactions of the intermediate peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low NO_x levels. These include bimolecular reactions with HO_2 and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products. Unimolecular isomerization reactions may also be available for complex peroxy radical intermediates. Capouet et al. (2004) calculated that peroxy radical (III) undergoes a ring closure reaction (forming a peroxide-bridged product) that dominates under most atmospheric conditions; and Berndt et al. (2016) have postulated that auto-oxidation reaction sequences, initiated by isomerization of peroxy radical (III) and involving a number of subsequent peroxy radical isomerization reactions, may account for the observed rapid formation of highly oxidized multifunctional organic compounds from the HO-initiated oxidation of α-pinene in chamber experiments. The role of unimolecular isomerization reactions has recently been confirmed by Xu et al. (2019), who experimentally and theoretically characterized a number of competitive ring-closure and H-atom shift reactions for peroxy radical (III).

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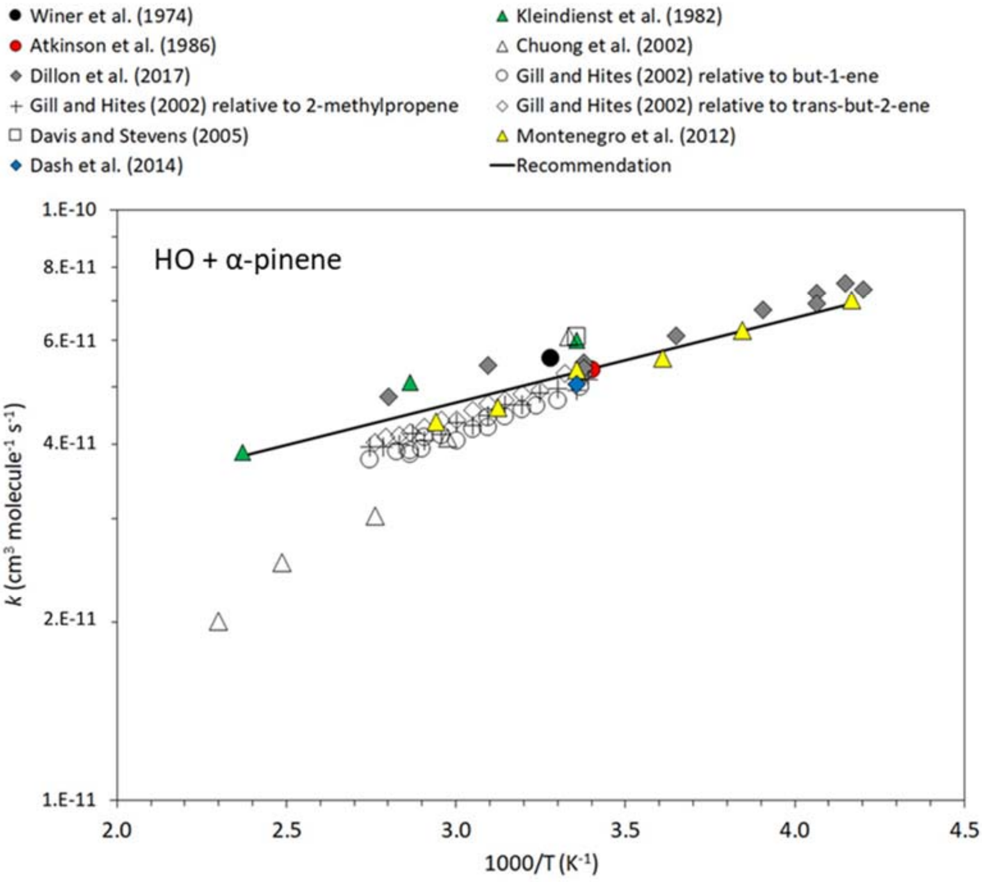

Rate coefficients for HO + α-pinene.

HOx_VOC14: *n*-butanal

Last evaluated: October 2007; Last change in preferred values: October 2007

HO + $CH_3CH_2CH_2CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$5.7 \times 10^{-12} \exp[(411 \pm 164)/T]$	258-422	Semmes et al., 1985	FP-RF
$(2.06 \pm 0.30) \times 10^{-11}$	298		
$(2.88 \pm 0.26) \times 10^{-11}$	298	Albaladejo et al., 2002	PLP-LIF
Relative Rate Coefficients			
$(2.31 \pm 0.06) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981	RR (a)
$(2.45 \pm 0.15) \times 10^{-11}$	296 ± 2	Papagni et al., 2000	RR (b)
$(2.39 \pm 0.16) \times 10^{-11}$	298 ± 2	D'Anna et al., 2001	RR (c)

Comments

(a) HO radicals were generated by the photolysis of HONO in air and the concentrations of butanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + butanal)/k(HO + ethene) = 2.96 ± 0.07 is placed on an absolute basis using k(HO + ethene) = 7.8×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of butanal and methyl vinyl ketone (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + butanal)/k(HO + methyl vinyl ketone) = 1.20 ± 0.07 is placed on an absolute basis using k(HO + methyl vinyl ketone) = 2.04×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of butanal and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of k(HO + butanal)/k(HO + 1-butene) = 0.76 ± 0.05 is placed on an absolute basis using k(HO + 1-butene) = 3.14×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (Atkinson, 1997; IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.3×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$5.8 \times 10^{-12} \exp(410/T)$	250-430
Reliability		
$\Delta \log k$	± 0.08	298
Δ E/R	± 250	250-430

Comments on Preferred Values

The preferred 298 K rate coefficient is the unweigthed mean of the room temperature absolute rate coefficient of Semmes et al. (1985) and the relative rate coefficients of Kerr and Sheppard (1981), Papagni et al. (2000) and D'Anna et al. (2001). The temperature dependence is that measured by Semmes et al. (1985), with the pre-exponential factor being adjusted to fit the 298 K preferred value. The room temperature rate coefficient of Albaladejo et al. (2002) is in good agreement with the preferred value. The relative rate coefficient of Audley et al. (1981) has not been used in the evaluation because, while it is in good agreement with the preferred 298 K rate coefficient, the rate coefficients of Audley et al. (1981) for 2-methyl-1-propanal, 1-pentanal and 2,2-dimethyl-1-propanal are significantly lower than the values of Semmes et al. (1985) and Kerr and Sheppard (1981). At room temperature and below, the reaction is expected to proceed primarily by H-atom abstraction from the -CHO group.

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HOx_VOC15: methacrolein

Last evaluated: October 2007; Last change in preferred values: October 2007

$HO + CH_2=C(CH_3)CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.77 \times 10^{-11} \exp[(175 \pm 52)/T]$	300-423	Kleindienst et al., 1982	FP-RF
$(3.14 \pm 0.49) \times 10^{-11}$	300		
$7.73 \times 10^{-12} \exp[(379 \pm 46)/T]$	234-373	Gierczak et al., 1997	PLP-LIF
$(2.79 \pm 0.12) \times 10^{-11}$	298		
$9.8 \times 10^{-13} \exp[(1050 \pm 120)/T]$	300-422	Chuong and Stevens, 2003	DF-RF/LIF (a)
$(3.23 \pm 0.36) \times 10^{-11}$	300		
$(3.22 \pm 0.10) \times 10^{-11}$	300	Chuong and Stevens, 2004	DF-LIF (b)
Relative Rate Coefficients			
$(3.23 \pm 0.24) \times 10^{-11}$	299 ± 2	Atkinson et al., 1983	RR (c)
$(3.90 \pm 0.31) \times 10^{-11}$	298 ± 2	Edney et al., 1986	RR (d)

Comments

(a) No variation in the rate coefficient was observed over the pressure range 2.7-6.7 mbar (2-5 Torr) of He diluent at any of the temperatures studied (300-422 K). The cited temperature-dependent rate expression uses data at 6.7 mbar (5.0 Torr) pressure of He (Chuong and Stevens, 2003). Problems ascribed to reversible wall adsorption of methacrolein and heterogeneous wall reactions were observed; these were avoided or minimized by addition of ~10% O_2 or by conditioning the reactor with high F atom concentrations

(b) At 133 mbar (100 Torr) of N_2 diluent, using a turbulent flow reactor.

(c) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + methacrolein)/k(HO + propene) = 1.13 ± 0.09 is placed on an absolute basis by using a rate coefficient of k(HO + propene) = 2.86×10^{-11} cm^3 molecule^{-1} s^{-1} at 299 K and atmospheric pressure of air (IUPAC, 2019).

(d) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene and *trans*-2-butene (the reference compounds) were measured by GC. The measured rate coefficient ratios are placed on an absolute basis using k(HO + propene) = 2.63×10^{-11} and k(HO + *trans*-2-butene) = 6.40×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure of air (UPAC, 2019). The indicated uncertainty is one standard deviation.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.0×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$8.4 \times 10^{-12} \exp(380/T)$	230-380
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 100	230-380

Comments on Preferred Values

The room temperature rate coefficients of Kleindienst et al. (1982), Atkinson et al. (1983), Gierczak et al. (1997) and Chuong and Stevens (2003, 2004) are in good agreement, with the relative rate measurement of Edney et al. (1986) being ~20-30% higher. The temperature dependencies obtained by Kleindienst et al. (1982) [300-423 K] and Chuong and Stevens (2003) [300-422 K] are respectively lower and higher than that determined by Gierczak et al. (1997) over the wider temperature range of 234-373 K. In the Chuong and Stevens (2003) study, the rate coefficients at 300, 328 and 361 K are in good agreement with the rate expression of Gierczak et al. (1997); those at 390 and 422 K (Chuong and Stevens, 2003) are lower than predicted from the Arrhenius expression of Gierczak et al. (1997). Because of the wider temperature range used by Gierczak et al. (1997) and the fact that it extends below room temperature, the temperature dependence of Gierczak et al. (1997) is accepted. The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983) and Gierczak et al. (1997), and the pre-exponential factor is calculated from the preferred 298 K rate coefficient and the temperature dependence.

The products of the reaction of HO radicals with methacrolein in the presence of NO have been investigated by Tuazon and Atkinson (1990) and Orlando and Tyndall (1999). The reaction proceeds by two pathways: H-atom abstraction from the CHO group, and initial addition of the HO radical to the carbon atoms of the C=C bond. H-atom abstraction from the CHO group accounts for 50-55% of the overall reaction at room temperature (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999), forming the acyl radical $CH_2=C(CH_3)CO$ which then adds O_2 to form the acyl peroxy radical $CH_2=C(CH_3)C(O)OO$. This acyl peroxy radical reacts with NO_2, to form the peroxyacyl nitrate $CH_2=C(CH_3)C(O)OONO_2$ (MPAN), or with NO (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999):

$$CH_2=C(CH_3)C(O)OO + NO_2 \rightarrow CH_2=C(CH_3)C(O)OONO_2$$
$$CH_2=C(CH_3)C(O)OO + NO \rightarrow CH_2=CCH_3 + CO_2 + NO_2$$

The $CH_2=CCH_3$ radical reacts with O_2 to form HCHO, CO and CO_2 (Orlando and Tyndall, 1999).

Initial HO radical addition to the C=C bond leads (in the presence of NO) to the intermediate hydroxyalkoxy radicals $HOCH_2C(O)(CH_3)CHO$ and $OCH_2C(OH)(CH_3)CHO$, which decompose by the pathways (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999):

$$HOCH_2C(O)(CH_3)CHO \rightarrow CH_3C(O)CHO + CH_2OH$$
$$HOCH_2C(O)(CH_3)CHO \rightarrow HOCH_2C(O)CH_3 + HCO$$

and

$$OCH_2C(OH)(CH_3)CHO \rightarrow HCHO + CH_3C(OH)CHO$$

followed by reactions of CH_2OH and $CH_3C(OH)CHO$ radicals with O_2 to form HCHO + HO_2 and $CH_3C(O)CHO$ + HO_2, respectively. The HO radical addition reaction appears to be in the high-pressure region above ~2.7 mbar (2 Torr) pressure (Gierczak et al., 1997; Chuong and Stevens, 2003). The first generation products from the HO radical addition pathways are therefore HCHO + $CH_3C(O)CHO$ and $HOCH_2C(O)CH_3$ + CO (the CO arising from reaction of HCO with O_2). The studies of Tuazon and Atkinson (1990) and Orlando and Tyndall (1999) measured formation yields of methylglyoxal and hydroxyacetone of 8.4% and 44%, respectively, showing that initial HO radical addition occurs mainly at the terminal CH_2 moiety (Tuazon and Atkinson, 1990).

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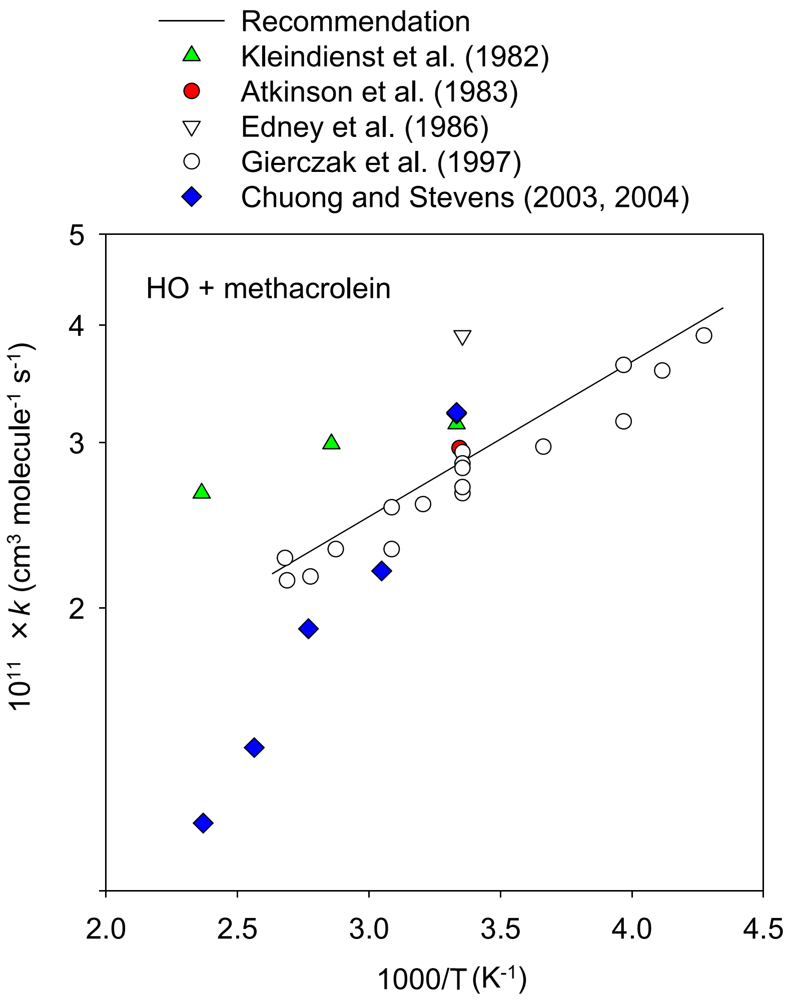

Rate coefficients for HO + methacrolein.

HO + $CH_3C(O)CH_2CH_3$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.3 \times 10^{-12} \exp[-(170 \pm 120)/T]$	240-440	Wallington and Kurylo, 1987	FP-RF
$(1.15 \pm 0.10) \times 10^{-12}$	296		
$1.51 \times 10^{-12} \exp[-(60 \pm 61)/T]$	243-372	Le Calvé et al., 1998	PLP-LIF
$(1.19 \pm 0.18) \times 10^{-12}$	298		
$1.35 \times 10^{-12} \exp[-(78 \pm 52)/T]$	228-388	Jiménez et al., 2005	PLP-LIF
$(1.04 \pm 0.07) \times 10^{-12}$	298		
$3.84 \times 10^{-24}\, T^4 \exp[(1038 \pm 11)/T]$	213-598	Carr et al., 2008	PLP-LIF
$(1.06 \pm 0.06) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(3.4 \pm 1.0) \times 10^{-12}$	305 ± 2	Winer et al., 1976	RR (a)
2.52×10^{-12}	300	Cox et al., 1980	RR (b)
$(8.7 \pm 0.9) \times 10^{-13}$	295 ± 2	Cox et al., 1981	RR (b)
$(9.1 \pm 1.6) \times 10^{-13}$	297	Edney et al., 1986	RR (c)

Comments

(a) HO radicals were generated by the photolysis of NO_x-organic-air mixtures, and the concentrations of 2-butanone and 2-methylpropene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 2-butanone)/k(HO + 2-methylpropene) = 0.07 (±30%) is placed on an absolute basis using k(HO + 2-methylpropene) = 4.92×10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of HONO in air, and the concentrations of 2-butanone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratios k(HO + 2-butanone)/k(HO + ethene) are placed on an absolute basis by use of rate coefficients at atmospheric pressure of k(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and 7.91×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K (IUPAC, 2019).

(c) HO radicals were generated from the photolysis of CH_3ONO in air, and the concentrations of 2-butanone and propane (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 2-butanone)/k(HO + propane) is placed on an absolute basis using k(HO + propane) = 1.07×10^{-12} cm^3 molecule^{-1} s^{-1} at 297 K (IUPAC, 2019).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.1×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	$1.5 \times 10^{-12} \exp(-90/T)$	210-300
Reliability		
$\Delta \log k$	± 0.10	298
$\Delta E/R$	± 200	210-300

Comments on Preferred Values

The measured rate coefficients exhibit a significant amount of scatter, ranging from $\sim 9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} to $\sim 1.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. The absolute rate coefficients of Wallington and Kurylo (1987) and Le Calvé et al. (1998) are higher than those of Jiménez et al. (2005) and Carr et al. (2008), and this difference becomes more pronounced at lower temperatures (<295 K). Photolysis of 2-butanone may have contributed to the measured 2-butanone loss rates in the relative rate studies of Winer et al. (1976) and Cox et al. (1980). The rate coefficients of Wallington and Kurylo (1987), Le Calvé et al. (1998) and Carr et al. (2008) suggest curvature in the Arrhenius plot. An un-weighted least-squares analysis of the absolute rate coefficients of Wallington and Kurylo (1987), Le Calvé et al. (1998), Jiménez et al. (2005) and Carr et al. (2008), using the three-parameter expression $k = CT^2 \exp(-D/T)$, results in $k = 3.28 \times 10^{-18}\ T^2 \exp(402/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 213-598 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 245 K and is derived from the above three-parameter expression with $A = C\, e^2 T^2$ and $B = D + 2T$.

Cox et al. (1981) observed acetaldehyde as a product of the HO radical reaction with 2-butanone, with a formation yield of 0.62 ± 0.02. Acetaldehyde is expected to arise from 2-butanone after H-atom abstraction from the CH_2 group, and hence the fraction of the overall HO radical reaction with 2-butanone proceeding via

$$HO + CH_3C(O)CH_2CH_3 \rightarrow H_2O + CH_3C(O)CHCH_3$$

is ~0.62.

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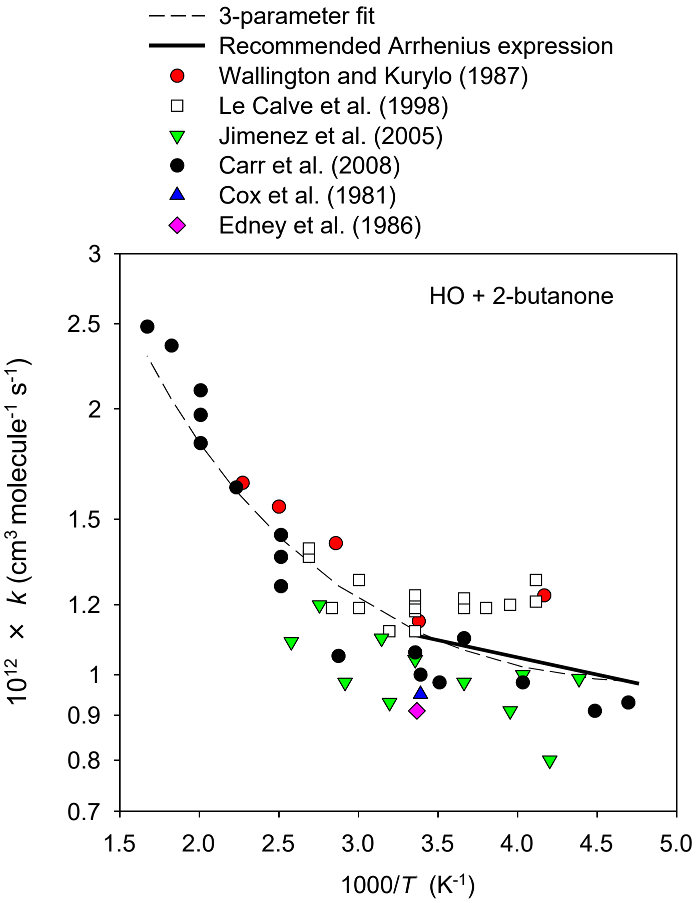

Rate coefficients for HO + 2-butanone.

HOx_VOC21: methyl vinyl ketone

Last evaluated: October 2007; Last change in preferred values: October 2007

HO + $CH_3C(O)CH{=}CH_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$3.85 \times 10^{-12} \exp[(456 \pm 73)/T]$	298-424	Kleindienst et al., 1982	FP-RF
$(1.79 \pm 0.28) \times 10^{-11}$	298		
$2.67 \times 10^{-12} \exp[(612 \pm 49)/T]$	232-378	Gierczak et al., 1997	PLP-LIF
$(2.03 \pm 0.17) \times 10^{-11}$	298		
$(1.73 \pm 0.21) \times 10^{-11}$	300	Chuong and Stevens, 2003	DF-RF/LIF (a)
$(1.78 \pm 0.08) \times 10^{-11}$	300	Chuong and Stevens, 2004	DF-LIF (b)
$(1.86 \pm 0.12) \times 10^{-11}$	298 ± 2	Holloway et al., 2005	PLP-LIF (c)
Relative Rate Coefficients			
1.36×10^{-11}	300	Cox et al., 1980	RR (d)
$(2.13 \pm 0.15) \times 10^{-11}$	299 ± 2	Atkinson et al., 1983	RR (e)

Comments

(a) At 300 K no measurable variation in the rate coefficient was observed over the pressure range 2.7-6.7 mbar (2-5 Torr) of He diluent; the cited rate coefficient is that obtained at 6.7 mbar (5 Torr) of He diluent. However, at the other temperatures studied (328, 361, 390 and 422 K) the measured rate coefficients increased with increasing pressure over the range 2.7-6.7 mbar (2-5 Torr) of He, showing that the reaction was in the fall-off regime under these temperature and pressure conditions. Problems ascribed to reversible wall adsorption of methyl vinyl ketone and heterogeneous wall reactions were observed; these were avoided or minimized by addition of ~10% O_2 or by conditioning the reactor with high F atom concentrations

(b) At 133 mbar (100 Torr) of N_2 diluent, using a turbulent flow reactor.

(c) The pulsed laser photolysis of 3-methyl-2,4-dione at 248 nm was used to generate HO radicals.

(d) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio is placed on an absolute basis using k(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air (IUPAC, 2019).

(e) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and propene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + methyl vinyl ketone)/k(HO + propene) = 0.747 ± 0.055 is placed on an absolute basis using k(HO + propene) = 2.85×10^{-11} cm^3 molecule^{-1} s^{-1} at 299 K and atmospheric pressure of air (IUPAC, 2019).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	2.0×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$2.6 \times 10^{-12} \exp(610/T)$	230-380
Reliability		
$\Delta \log k$	± 0.10	298
$\Delta E/R$	± 200	230-380

Comments on Preferred Values

The room temperature rate coefficients of Kleindienst et al. (1982), Atkinson et al. (1983), Gierczak et al. (1997), Chuong and Stevens (2003, 2004) and Holloway et al. (2005) are in good agreement, but are higher by ~20-35% than the earlier relative rate measurement of Cox et al. (1980). The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983), Gierczak et al. (1997) and Holloway et al. (2005). The temperature dependence measured by Gierczak et al. (1997) is accepted and the pre-exponential factor is calculated from the preferred 298 K rate coefficient and the temperature dependence.

The products of the reaction of HO radicals with methyl vinyl ketone in the presence of NO have been investigated by Tuazon and Atkinson (1989). The reaction proceeds by initial addition of the HO radical to the carbon atoms of the C=C bond, forming (in the presence of NO) the intermediate hydroxyalkoxy radicals $CH_3C(O)CH(O)CH_2OH$ and $CH_3C(O)CH(OH)CH_2O$, which decompose by the pathways:

$$CH_3C(O)CH(O)CH_2OH \rightarrow CH_3C(O)CHO + CH_2OH$$
$$CH_3C(O)CH(O)CH_2OH \rightarrow CH_3CO + HOCH_2CHO$$

and

$$CH_3C(O)CH(OH)CH_2O \rightarrow HCHO + CH_3C(O)CHOH$$

followed by reactions of CH_2OH and $CH_3C(O)CHOH$ radicals with O_2 to form HCHO + HO_2 and $CH_3C(O)CHO$ + HO_2, respectively. The first generation products are therefore HCHO + $CH_3C(O)CHO$ and $HOCH_2CHO$ + CH_3CO (with the acetyl radical reacting to form peroxyacetyl nitrate [$CH_3C(O)OONO_2$; PAN] or HCHO (Tuazon and Atkinson, 1989; IUPAC, 2019)). Tuazon and Atkinson (1989) measured formation yields of methylglyoxal and glycolaldehyde of 25 ± 8% and 64 ± 16%, respectively, showing that initial HO radical addition occurs mainly at the terminal CH_2 group (Tuazon and Atkinson, 1989).

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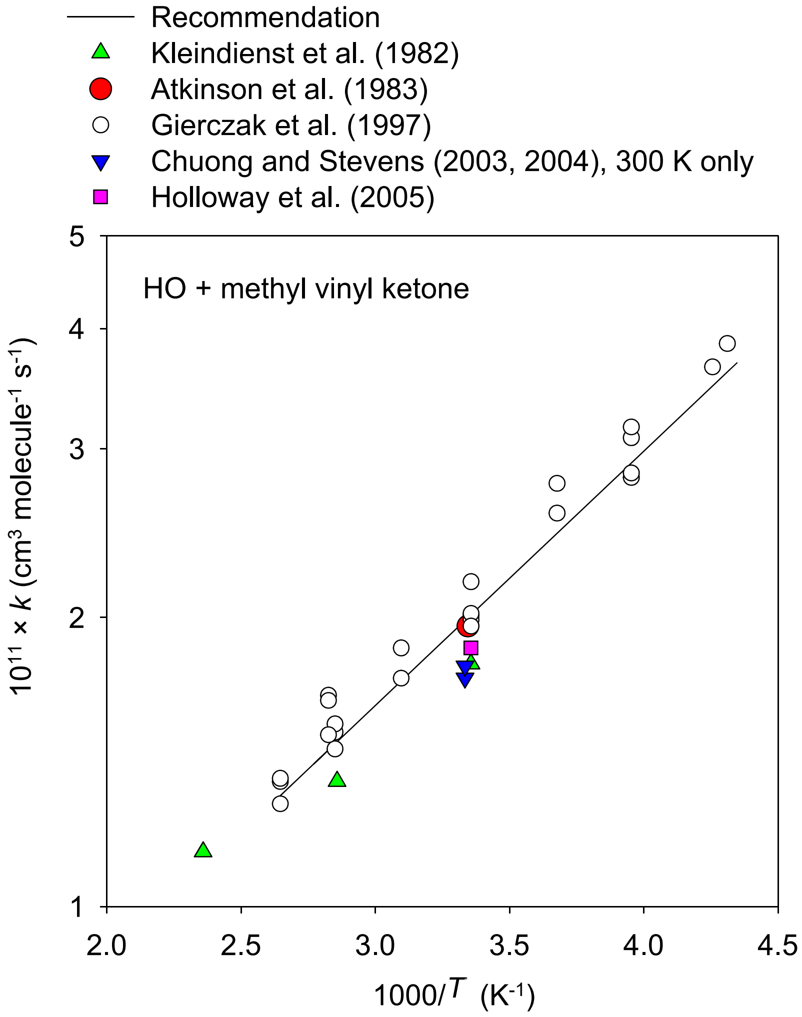
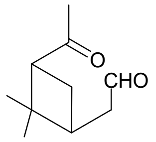


Rate coefficients for HO + methyl vinyl ketone.

HOx_VOC22: pinonaldehyde

Last evaluated: December 2007; Last change in preferred values: December 2007

HO +



→ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$4.5 \times 10^{-12} \exp[(600 \pm 100)/T]$	297-374	Davis et al., 2007	PLP-LIF (a)
$(3.46 \pm 0.52) \times 10^{-11}$	297		
Relative Rate Coefficients			
$(9.48 \pm 1.14) \times 10^{-11}$	298 ± 2	Hallquist et al., 1997	RR (b)
$(8.9 \pm 2.6) \times 10^{-11}$	300 ± 5	Glasius et al., 1997	RR (c,d)
$(9.0 \pm 1.3) \times 10^{-11}$	300 ± 5	Glasius et al., 1997	RR (c,e)
$(4.5 \pm 0.8) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (f,g)
$(4.9 \pm 1.1) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (f,h)
$(5.4 \pm 0.9) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (f,i)
$(3.0 \pm 0.8) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (d,j)
$(5.5 \pm 1.5) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (e,j)
$(4.7 \pm 0.6) \times 10^{-11}$	295 ± 3		
$(2.8 \pm 1.0) \times 10^{-11}$	295 ± 3		
$(2.7 \pm 0.6) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (j,k)
$(3.3 \pm 0.3) \times 10^{-11}$	295 ± 3		
$(2.8 \pm 0.3) \times 10^{-11}$	295 ± 3		
$(3.9 \pm 0.4) \times 10^{-11}$	295 ± 3		
$(3.7 \pm 1.1) \times 10^{-11}$	299 ± 2	Nozière et al., 1999	RR (k,l)
$(4.2 \pm 1.1) \times 10^{-11}$	290 ± 2		
$(3.8 \pm 1.5) \times 10^{-11}$	288 ± 1		
$(4.4 \pm 0.8) \times 10^{-11}$	287 ± 1		
$(4.4 \pm 1.0) \times 10^{-11}$	289 ± 2		

Pinonaldehyde is 3-acetyl-2,2-dimethyl-cyclobutaneacetaldehyde,

Comments

(a) Pinonaldehyde was measured by UV absorption at 185 nm before and after gas mixtures flowed through the reaction vessel and by IR absorption before the reaction vessel. The cited error in the 297 K rate coefficient is the estimated overall uncertainty (±15%).

(b) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at 1013 ± 5 mbar (760 ± 3.8) pressure. The concentrations of pinonaldehyde and propene (the reference compound) were measured by FTIR spectroscopy. Wall losses of pinonaldehyde in the 153 L chamber were observed and measured in separate experiments and taken into account in the data analysis. The measured rate coefficient ratio of k(HO + pinonaldehyde)/k(HO + propene) is placed on an absolute basis using a rate coefficient at 298 K and atmospheric pressure of air of k(HO + propene) = 2.86×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of CH_3ONO-NO-air or H_2O_2-air mixtures at

987 ± 7 mbar (740 ± 5 Torr) pressure. The concentrations of pinonaldehyde and isoprene or 1,3-butadiene (the reference compounds) were measured by FTIR spectroscopy. Decays of pinonaldehyde in the dark and due to photolysis were observed in the 480 L reaction chamber used and were taken into account in the data analysis. The measured rate coefficient ratios of *k*(HO + pinonaldehyde)/*k*(HO + isoprene) = 0.896 ± 0.260 and *k*(HO + pinonaldehyde)/*k*(HO + 1,3-butadiene) = 1.37 ± 0.19 are placed on an absolute basis using rate coefficients at 300 K of *k*(HO + isoprene) = 9.91×10^{-11} (IUPAC, 2019) and *k*(HO + 1,3-butadiene) = 6.59×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(d) Relative to *k*(HO + isoprene).

(e) Relative to *k*(HO + 1,3-butadiene).

(f) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at 987 mbar (740 Torr) pressure. The concentrations of pinonaldehyde and propene, 1-butene or *m*-xylene (the reference compounds) were measured by GC. No measurable decays (<5%) of pinonaldehyde were observed due to dark decays to the walls of the 7000 L Teflon chamber used or due to photolysis at wavelengths >300 nm. The measured rate coefficient ratios of *k*(HO + pinonaldehyde)/*k*(HO + propene) = 1.70 ± 0.29, *k*(HO + pinonaldehyde)/*k*(HO + 1-butene) = 1.56 ± 0.33 and *k*(HO + pinonaldehyde)/*k*(HO + *m*-xylene) = 2.35 ± 0.35 are placed on an absolute basis using rate coefficients at 296 K and atmospheric pressure of air of *k*(HO + propene) = 2.88×10^{-11}, *k*(HO + 1-butene) = 3.17×10^{-11}, and *k*(HO + *m*-xylene) = 2.31×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

(g) Relative to *k*(HO + propene).

(h) Relative to *k*(HO + 1-butene).

(i) Relative to *k*(HO + *m*-xylene).

(j) HO radicals were generated by the photolysis of CH_3ONO-NO-air or H_2O_2-air mixtures at 1013 mbar (760 Torr) pressure. The concentrations of pinonaldehyde and reference compound (isoprene, 1,3-butadiene or cyclohexane) were measured by FTIR spectroscopy. Wall losses and photolysis was observed in the various chambers used (ranging from 405 to 1080 L volume) and were taken into account in the data analysis. The measured rate coefficient ratios of *k*(HO + pinonaldehyde)/*k*(HO + isoprene), *k*(HO + pinonaldehyde)/*k*(HO + 1,3-butadiene) and *k*(HO + pinonaldehyde)/*k*(HO + cyclohexane) are placed on an absolute basis using rate coefficients at 295 K of *k*(HO + isoprene) = 1.01×10^{-11} (IUPAC, 2019), *k*(HO + 1,3-butadiene) = 6.76×10^{-11} (Atkinson and Arey, 2003), and *k*(HO + cyclohexane) = 6.90×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 2003; Atkinson and Arey, 2003).

(k) Relative to *k*(HO + cyclohexane).

(l) Experiments carried out in the ~180000 L volume EUPHORE chamber with HO radicals being generated by the dark reaction of ozone with 2,3-dimethyl-2-butene in air at ~1 bar pressure. The concentrations of pinonaldehyde and cyclohexane were monitored during the experiments by FTIR spectroscopy (pinonaldehyde and cyclohexane) and also by HPLC after derivatization for pinonaldehyde and by GC for cyclohexane. The measured rate coefficient ratios of *k*(HO + pinonaldehyde)/*k*(HO + cyclohexane) are placed on an absolute basis using *k*(HO + cyclohexane) = $3.26 \times 10^{-17} T^2 \exp(262/T)$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 2003; Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.9×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$5.2 \times 10^{-12} \exp(600/T)$	230-380
Reliability		
$\Delta \log k$	± 0.15	298
$\Delta E/R$	± 300	230-380

Comments on Preferred Values

Pinonaldehyde is a low volatility product of the atmospheric reactions of α-pinene. Pinonaldehyde is prone to wall losses, making measurement of its reaction rate coefficients difficult. The available rate coefficients are from four relative rate studies carried out at around room temperature and a recent absolute rate study carried out over the temperature range 297-374 K (Hallquist et al., 1997; Glasius et al., 1997; Alvarado et al., 1998; Nozière et al., 1999; Davis et al., 2007). At room temperature the measured rate coefficients range over a factor of ~3, with those measured by Hallquist et al. (1997) and Glasius et al. (1997) being a factor of ~2 higher than those of Alvarado et al. (1998), Nozière et al. (1999) and Davis et al. (2007), possibly because of unresolved wall adsorption problems. The preferred values are based on the absolute rate study of Davis et al. (2007) and the relative rate studies of Alvarado et al. (1998), carried out in a large volume Teflon chamber, and Nozière et al. (1999), carried out in various chambers of volume ranging from 405 L to ~180000 L. After correction to 298 K using the temperature dependence of Davis et al. (2007), the rate coefficients measured by Alvarado et al. (1998) have been aggregated into an average of 4.9×10^{-11} cm^3 molecule^{-1} s^{-1}, and those measured in the extensive study of Nozière et al. (1999) have been aggregated into an average rate coefficient from the indoor chambers with photolytic production of HO radicals of 3.5×10^{-11} cm^3 molecule^{-1} s^{-1} and an average rate coefficient from the EUPHORE chamber study (with dark production of HO radicals) of 3.9×10^{-11} cm^3 molecule^{-1} s^{-1}. A simple average of these three relative rate coefficients and the absolute rate coefficient of Davis et al. (2007) (corrected to 298 K as described above), which are in agreement within their experimental uncertainties, leads to the preferred 298 K rate coefficient. The temperature dependence of Davis et al. (2007) is accepted and combined with the preferred 298 K rate coefficient to derive the pre-exponential factor.

The reaction proceeds by H-atom abstraction from the various C-H bonds, including from the CHO group. By analogy with other aldehydes (IUPAC, 2019), the negative temperature dependence suggests that a substantial fraction of the reaction proceeds by H-atom abstraction from the CHO group.

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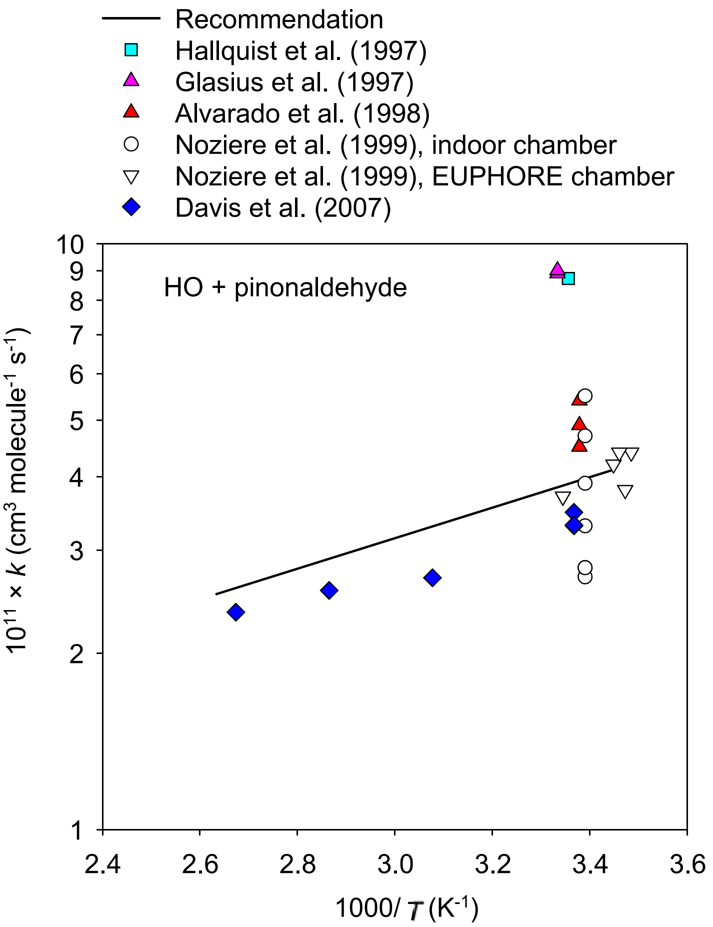

Rate coefficients for HO + pinonaldehyde.

HOx_VOC27: 1-butanol

Last evaluated: August 2007; Last change in preferred values: August 2007

$HO + CH_3CH_2CH_2CH_2OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(8.31 \pm 0.63) \times 10^{-12}$	296	Wallington and Kurylo, 1987	FP-RF
$(7.80 \pm 0.20) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
$5.30 \times 10^{-12} \exp[(146 \pm 92)/T]$	263-372	Mu and Mellouki, 2001	PLP-LIF
$(8.47 \pm 0.34) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(6.8 \pm 1.3) \times 10^{-12}$	292	Campbell et al., 1976	RR (a)
$(7.97 \pm 0.66) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (b)
$(1.03 \pm 0.05) \times 10^{-11}$	298 ± 2	Oh and Andino, 2001	RR (c)
$(7.67 \pm 0.14) \times 10^{-12}$	298 ± 2	Cavalli et al., 2002	RR (b)
$(8.58 \pm 0.66) \times 10^{-12}$	295 ± 2	Wu et al., 2003	RR (d)

Comments

(a) HO radicals were generated by the dark reaction of H_2O_2-NO_2 mixtures in the presence of CO and an organic compound. From sequential experiments using *n*-butane and 1-butanol, a rate coefficient ratio of k(HO + 1-butanol)/k(HO + *n*-butane) = 3.00 ± 0.56 (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis using k(HO + *n*-butane) = 2.28×10^{-12} cm^3 molecule^{-1} s^{-1} at 292 K (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + 1-butanol)/k(HO + cyclohexane) is placed on an absolute basis using k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003) [Cavalli et al. (2002) measured a rate coefficient ratio of k(HO + 1-butanol)/k(HO + cyclohexane) = 1.10 ± 0.02].

(c) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-butanol and *p*-xylene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + 1-butanol)/k(HO + *p*-xylene) = 0.72 ± 0.03 is placed on an absolute basis using k(HO + *p*-xylene) = 1.43×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (Calvert et al., 2002).

(d) HO radicals were generated by the photolysis of H_2O_2 in 1 atmosphere of air at 254 nm. The concentrations of 1-butanol and propane (the reference compound) were measured by GC. The measured rate coefficient ratio, k(HO + 1-butanol)/k(HO + propane), is placed on an absolute basis using k(HO + propane) = 1.07×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K (Atkinson, 2003; IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	8.5×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	$5.3 \times 10^{-12} \exp(140/T)$	260-380
Reliability		
$\Delta \log k$	± 0.06	298
Δ E/R	± 200	260-380

Comments on Preferred Values

The absolute rate study of Mu and Mellouki (2001), the sole temperature-dependence study, is used to derive the preferred values. The 298 K coefficient from the study of Yujing and Mellouki (2001) is in good agreement with the room temperature absolute and relative rate coefficients of Wallington and Kurylo (1987), Nelson et al. (1990), Cavalli et al. (2002) and Wu et al. (2003), but is 18% lower than the relative rate coefficient of Oh and Andino (2001).

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HOx_VOC28: 2-butanol

Last evaluated: August 2007; Last change in preferred values: August 2007

HO + $CH_3CH(OH)CH_2CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(8.58 \pm 0.49) \times 10^{-12}$	296 ± 2	Chew and Atkinson, 1996	RR (a)
$(8.80 \pm 0.14) \times 10^{-12}$	297 ± 3	Baxley and Wells, 1998	RR (b,c)
$(7.57 \pm 0.44) \times 10^{-12}$	297 ± 3	Baxley and Wells, 1998	RR (b,d)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 2-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 2-butanol)/k(HO + cyclohexane) = 1.24 ± 0.07 is placed on an absolute basis using k(HO + cyclohexane) = 6.92×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 2003).

(b) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 2-butanol and *n*-nonane and *n*-dodecane (the reference compounds) were measured by GC. The measured rate coefficient ratios of k(HO + 2-butanol)/k(HO + *n*-nonane) and k(HO + 2-butanol)/k(HO + *n*-dodecane) are placed on an absolute basis by use of rate coefficients at 297 K of k(HO + *n*-nonane) = 9.69×10^{-12} and k(HO + *n*-dodecane) = 1.32×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson, 2003).

(c) Relative to HO + *n*-nonane.

(d) Relative to HO + *n*-dodecane.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	8.7×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.08	298

Comments on Preferred Values

The preferred value is based on the relative rate coefficient of Chew and Atkinson (1996) and that of Baxley and Wells (1998) relative to HO + *n*-nonane, which are in excellent agreement. The rate coefficient of Baxley and Wells (1998) measured relative to that for HO + *n*-dodecane, while in agreement with the other two rate coefficients (Chew and Atkinson, 1996; Baxley and Wells, 1998), is more uncertain because of the small data-base for HO + *n*-dodecane (Atkinson, 2003), and hence this rate coefficient is not used in the evaluation.

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HOx_VOC29: 2-methyl-3-buten-2-ol

Last evaluated: Octobert 2007; Last change in preferred values: October 2007

$HO + (CH_3)_2C(OH)CH=CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Technique/ Comments
Absolute Rate Coefficients			
8.2×10^{-12} exp[$(610 \pm 50)/T$]	231-300	Rudich et al., 1995	PLP-LIF (a)
$(6.4 \pm 0.6) \times 10^{-11}$	298		
$(6.32 \pm 0.27) \times 10^{-11}$	300	Baasandorj and Stevens, 2007	DF-LIF (b)
Relative Rate Coefficients			
$(3.81 \pm 0.80) \times 10^{-11}$	298 ± 2	Fantechi et al., 1998a	RR (c,d)
$(4.64 \pm 1.80) \times 10^{-11}$	298 ± 2	Fantechi et al., 1998a	RR (c,e)
$(6.93 \pm 0.54) \times 10^{-11}$	295 ± 1	Ferronato et al., 1998	RR (e,f)
$(6.72 \pm 0.78) \times 10^{-11}$	295 ± 1	Ferronato et al., 1998	RR (f,g)
$(5.64 \pm 0.13) \times 10^{-11}$	296 ± 2	Papagni et al., 2001	RR (h)
$(7.01 \pm 0.28) \times 10^{-11}$	298 ± 2	Imamura et al., 2004	RR (i,j)
$(7.03 \pm 0.32) \times 10^{-11}$	298 ± 2	Imamura et al., 2004	RR (e,i)
$(5.6 \pm 0.2) \times 10^{-11}$	298 ± 2	Carrasco et al., 2007	RR (d,i)

Comments

(a) Rate coefficients for the reactions of HO, $H^{18}O$ and DO radicals with 2-methyl-3-buten-2-ol were measured, in the presence and absence of O_2 [up to 13.5 Torr (18 mbar) O_2 in the case of the HO radical reaction], over the temperature range 231-410 K. Above ~350 K the rate coefficients decreased with increasing temperature faster than predicted based on extrapolation of the lower temperature data. For the HO radical reaction, the rate coefficients in the presence of 2-13.5 Torr (2.7-18 mbar) of O_2 were up to 15-20% higher than in the absence of O_2, while the measured rate coefficients for the DO radical reaction were invariant to the presence or absence of O_2. HO radicals were observed to be formed in the DO radical reaction, and the rate coefficients of the DO radical and $H^{18}O$ radical reactions were essentially identical to those for the HO radical reactions in the presence of O_2. These data indicated that the measured rate coefficients from the HO radical reaction in the absence of O_2 are low because of HO radical regeneration, whereas $H^{18}O$ and DO radical regeneration does not occur from reactions of $H^{18}O$ and DO radicals with 2-methyl-3-buten-2-ol (HO radicals being formed by elimination of the –OH group in the 2-methyl-3-buten-2-ol in the absence of O_2). The rate coefficient cited is derived (Rudich et al., 1995) from the rate coefficients measured for the HO and DO radical reactions in the presence of O_2 over the temperature range 230-300 K, and is expected to be applicable to atmospheric conditions.

(b) Rate coefficients were measured over the temperature range 300-415 K at total pressures of helium diluent of 2-5 Torr (2.7-6.7 mbar), in the presence and absence of O_2. The room temperature rate coefficient measured in the presence of ~5-15% O_2 was ~15% higher than that measured in the absence of O_2 [as also observed by Rudich et al. (1995); see Comment (a)]. While the rate coefficient at 300 K was independent of total pressure over the range 2-5 Torr (2.7-6.7 mbar), at ≥335 K the measured rate coefficients in the presence of O_2 were pressure dependent. These observations indicate that at temperatures ≥335 K and pressures

<5 Torr (6.7 mbar) the reaction is in the fall-off regime. Hence only the 300 K pressure-independent rate coefficient is listed in the table. Rate coefficients were also measured for the reaction of DO radicals with 2-methyl-3-buten-2-ol over the same temperature range, with a 300 K rate coefficient of (6.61 ± 0.66) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1}.

(c) HO radicals were generated by the photolysis of H_2O_2 at 253.7 nm in air at 987 ± 7 (740 ± 5) mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and isoprene (or propene) [the reference compounds] were measured during the experiments by FTIR spectroscopy. The measured rate coefficient ratios *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + isoprene) and *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + propene) are placed on an absolute basis using rate coefficients at 298 K and atmospheric pressure of *k*(HO + isoprene) = 1.00 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003; IUPAC, 2019) and *k*(HO + propene) = 2.86 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

(d) Relative to *k*(HO + isoprene).

(e) Relative to *k*(HO + propene).

(f) HO radicals were generated by the photolysis (340-400 nm) of $^{13}CH_3ONO$-NO-$(CH_3)_2C(OH)CH{=}CH_2$-propene (or ethene) [the reference compounds]-air mixtures at 933 mbar (700 Torr) pressure. The concentrations of 2-methyl-3-buten-2-ol and propene (or ethene) were measured by FTIR spectroscopy. The measured rate coefficient ratios of *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + propene) = 2.4 ± 0.2 and *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + ethene) = 8.5 ± 0.9 are placed on an absolute basis using rate coefficients at 295 K and atmospheric pressure of air of *k*(HO + propene) = 2.89 × 10^{-11} and *k*(HO + ethene) = 7.91 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

(g) Relative to *k*(HO + ethene).

(h) HO radicals were generated by the photolysis (at ≥300 nm) of CH_3ONO-NO-$(CH_3)_2C(OH)CH{=}CH_2$-1,3,5-trimethylbenzene (the reference compound)-air mixtures at 987 mbar (740 Torr) pressure. The concentrations of 2-methyl-3-buten-2-ol and 1,3,5-trimethylbenzene were measured by GC. The measured rate coefficient ratio of *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + 1,3,5-trimethylbenzene) = 0.995 ± 0.022 is placed on an absolute basis using *k*(HO + 1,3,5-trimethylbenzene) = 5.67 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 296 K (Atkinson and Arey, 2003).

(i) HO radicals were generated by the photolysis of CH_3ONO-NO-$(CH_3)_2C(OH)CH{=}CH_2$-di-*n*-butyl ether, propene or isoprene (the reference compounds)-air mixtures at atmospheric pressure. The concentrations of 2-methyl-3-buten-2-ol and the reference compounds were measured by FTIR spectroscopy. The measured rate coefficient ratios of *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + di-*n*-butyl ether) = 2.32 ± 0.10 (Imamura et al., 2004), *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + propene) = 2.46 ± 0.12 (Imamura et al., 2004) and *k*(HO + 2-methyl-3-buten-2-ol)/*k*(HO + isoprene) = 0.56 ± 0.02 (Carrasco et al., 2007) are placed on an absolute basis using rate coefficients at 298 K and atmospheric pressure of air of *k*(HO + di-*n*-butyl ether) = 2.78 × 10^{-11} (Mellouki et al., 1995), *k*(HO + propene) = 2.86 × 10^{-11} (IUPAC, 2019), and *k*(HO + isoprene) = 1.00 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003; IUPAC, 2019).

(j) Relative to *k*(HO + di-*n*-butyl ether).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	6.5×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$8.4 \times 10^{-12} \exp(610/T)$	230-300
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 200	230-300

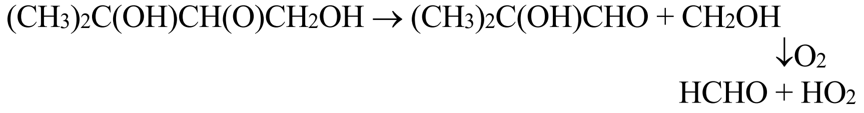
Comments on Preferred Values

The room temperature rate coefficients of Rudich et al. (1995), Ferronato et al. (1998), Papagni et al. (2001), Imamura et al. (2004), Baasandorj and Stevens (2007) and Carrasco et al. (2007) are in reasonable agreement, although the rate coefficient of Ferronato et al. (1998) relative to ethene is somewhat higher than those of Rudich et al. (1995), Papagni et al. (2001), Imamura et al. (2004), Baasandorj and Stevens (2007) and Carrasco et al. (2007) and that of Ferronato et al. (1998) relative to propene. The two relative rate coefficients of Fantechi et al. (1998a) are significantly lower than the values measured by Rudich et al. (1995), Ferronato et al. (1998), Papagni et al. (2001), Imamura et al. (2004), Baasandorj and Stevens (2007) and Carrasco et al. (2007). The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Rudich et al. (1995), Ferronato et al. (1998), Papagni et al. (2001), Imamura et al. (2004) and Carrasco et al. (2007). The preferred temperature dependence is that reported by Rudich et al. (1995), and the pre-exponential factor is adjusted to fit the preferred 298 K rate coefficient.

The reaction proceeds almost totally by initial addition of HO to the C=C bond (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003; Carrasco et al., 2007). In the presence of NO at atmospheric pressure of air the observed products are formaldehyde, acetone, glycolaldehyde, 2-hydroxy-2-methylpropanal [$(CH_3)_2C(OH)CHO$], and dihydroxynitrates [presumed to be $(CH_3)_2C(OH)CH(OH)CH_2ONO_2$ and $(CH_3)_2C(OH)CH(ONO_2)CH_2OH$] (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003; Carraso et al., 2007). Based on the product studies of Ferronato et al. (1998), Alvarado et al. (1999), Reisen et al. (2003) and Carrasco et al. (2007) carried out in the presence of NO, the product yields are: formaldehyde, 35 ± 4% (Ferronato et al., 1998), 29 ± 3% (Alvarado et al., 1999) and 33 ± 8% (Carrasco et al., 2007); acetone, 52 ± 5% (Ferronato et al., 1998), 58 ± 4% (Alvarado et al., 1999) and 67 ± 5% (Carrasco et al., 2007); glycolaldehyde, 50 ± 5% (Ferronato et al., 1998), 61 ± 9% (Alvarado et al., 1999) and 78 ± 20% (Carrasco et al., 2007); 2-hydroxy-2-methylpropanal, 31 ± 4% (Reisen et al., 2003) and 31 ± 11% (Carrasco et al., 2007) [note that Carrasco et al. (2007) had a standard of 2-hydroxy-2-methylpropanal available, in contrast to Riesen et al. (2003)]; and dihydroxynitrates, 5 ± 2% (Alvarado et al., 1999).

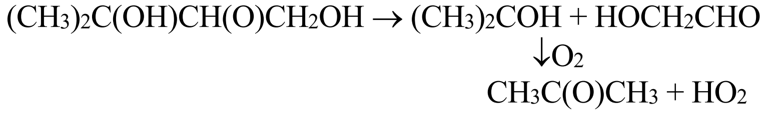
The reaction mechanism is discussed in detail in Alvarado et al. (1999) and Carrasco et al. (2007). Reactions of the $(CH_3)_2C(OH)CH(OH)CH_2OO$ and $(CH_3)_2C(OH)CH(OO)CH_2OH$ peroxy radicals (formed after addition of O_2 to the initially formed $(CH_3)_2C(OH)CH(OH)CH_2$ and $(CH_3)_2C(OH)CHCH_2OH$ radicals) with NO lead to the formation of the dihydroxynitrates $(CH_3)_2C(OH)CH(OH)CH_2ONO_2$ and $(CH_3)_2C(OH)CH(ONO_2)CH_2OH$ or NO_2 plus the dihydroxyalkoxy radicals $(CH_3)_2C(OH)CH(OH)CH_2O$ and $(CH_3)_2C(OH)CH(O)CH_2OH$. At room temperature and atmospheric pressure of air the dominant fate of these dihydroxyalkoxy radicals is decomposition:

$$\begin{array}{r} \mathrm{(CH_3)_2C(OH)CH(OH)CH_2O \rightarrow HCHO + (CH_3)_2C(OH)CHOH} \\ \downarrow \mathrm{O_2} \\ \mathrm{(CH_3)_2C(OH)CHO + HO_2} \end{array}$$



$$\begin{array}{r} \mathrm{(CH_3)_2C(OH)CH(O)CH_2OH \rightarrow (CH_3)_2C(OH)CHO + CH_2OH} \\ \downarrow \mathrm{O_2} \\ \mathrm{HCHO + HO_2} \end{array}$$

and/or



$$\begin{array}{l} \mathrm{(CH_3)_2C(OH)CH(O)CH_2OH \rightarrow (CH_3)_2COH + HOCH_2CHO} \\ \qquad\qquad\qquad\downarrow \mathrm{O_2} \\ \qquad\qquad\mathrm{CH_3C(O)CH_3 + HO_2} \end{array}$$

Hence, as observed, it is expected that HCHO and $(CH_3)_2C(OH)CHO$ will be formed in the same yield [~31%], and that $HOCH_2CHO$ and $CH_3C(O)CH_3$ will be formed in the same yield [~60%] (Ferronato et al., 1998; Alvarado et al., 1999; Reisen et al., 2003; Carrasco et al., 2007). Fantechi et al. (1998b) and Carrasco et al. (2007) have investigated the reaction in the absence of NO (see Carrasco et al., 2007, for details).

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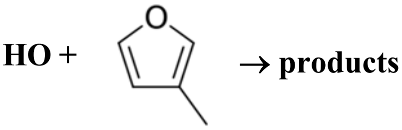
HOx_VOC31: 3-methylfuran

Last evaluated: December 2007; Last change in preferred values: December 2007



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(9.26 \pm 0.24) \times 10^{-11}$	296 ± 2	Atkinson et al., 1989	RR (a)

Comments

(a) Carried out at atmospheric pressure of air. HO radicals were generated by the photolysis of methyl nitrite-NO-air mixtures, and the concentrations of 3-methylfuran and 2,3-dimethyl-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + 3-methylfuran)/k(HO + 2,3-dimethyl-2-butene) = 0.842 ± 0.021 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.10×10^{-10} cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1997).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	9.3×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Atkinson et al. (1989). The reaction of HO radicals with 3-methylfuran is expected to proceed almost exclusively by initial HO radical addition to the C=C bonds (Atkinson et al., 1989).

References

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HOx_VOC33: 2-hydroxy-2-methylpropanal

Last evaluated: July 2007; Last change in preferred values: July 2007

HO + $(CH_3)_2C(OH)CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.49 \pm 0.21) \times 10^{-11}$	296 ± 2	Baker et al., 2004	RR (a)
$(1.36 \pm 0.14) \times 10^{-11}$	295 ± 2	Carrasco et al., 2006	RR (b)
$(1.23 \pm 0.06) \times 10^{-11}$	293 ± 2	Carrasco et al., 2006	RR (c)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at wavelengths >300 nm. $(CH_3)_2C(OH)CHO$ was generated in situ from the reaction of HO radicals with $(CH_3)_2C(OH)CH{=}CH_2$ and its concentration was measured during the reactions using solid phase microextraction fibers pre-coated with *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine for on-fiber derivatization of carbonyl compounds, with subsequent GC analyses. From the time-concentration behavior of $(CH_3)_2C(OH)CHO$ during the reactions, the rate coefficient ratio $k(HO + (CH_3)_2C(OH)CHO)/k(HO + (CH_3)_2C(OH)CH{=}CH_2) = 0.234 \pm 0.033$ was derived. This rate coefficient ratio is placed on an absolute basis using $k(HO + (CH_3)_2C(OH)CH{=}CH_2) = 6.36 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of HONO at ~420 nm in synthetic air at atmospheric pressure. A synthesized sample of $(CH_3)_2C(OH)CHO$ was used, and the concentrations of $(CH_3)_2C(OH)CHO$ and isoprene (the reference compound) were monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + (CH_3)_2C(OH)CHO)/k(HO + \text{isoprene}) = 0.135 \pm 0.014$ is placed on an absolute basis using $k(HO + \text{isoprene} = 1.01 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of H_2O_2 in air by natural sunlight in the EUPHORE chamber at atmospheric pressure. A synthesized sample of $(CH_3)_2C(OH)CHO$ was used, and the concentrations of $(CH_3)_2C(OH)CHO$ and di-*n*-butyl ether (the reference compound) were monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(HO + (CH_3)_2C(OH)CHO)/k(HO + \text{di-}n\text{-butyl ether}) = 0.43 \pm 0.02$ is placed on an absolute basis using $k(HO + \text{di-}n\text{-butyl ether}) = 2.87 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 293 K (Mellouki et al., 1995).

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	1.4×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Values

The two kinetic studies of this reaction are in good agreement, and the preferred value is the average of the three measurements, all of which are relative rate measurements using different reference compounds. Product studies show that acetone is formed in essentially 100% yield in both the presence and absence of NO, with molar yields of 1.06 ± 0.06 in the presence of NO and 1.10 ± 0.06 in the absence of NO (Carrasco et al., 2006). The reaction is expected to proceed mainly by H-atom abstraction from the –CHO group (Baker et al., 2004; Carrasco et al., 2006).

References

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Mellouki, A., Téton, S. and Le Bras, G.: Int. J. Chem. Kinet. 27, 791, 1995.

HOx_VOC42: 1-butyl nitrate

Last evaluated: July 2007; Last change in preferred values: July 2007

HO + 1-$C_4H_9ONO_2$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.74 \pm 0.19) \times 10^{-12}$	298 ± 2	Nielsen et al., 1991	PR-RA (a)
Relative Rate Coefficients			
$(1.31 \pm 0.10) \times 10^{-12}$	299 ± 2	Atkinson et al., 1982	RR (b,c)
$(1.65 \pm 0.18) \times 10^{-12}$	298 ± 2	Atkinson and Aschmann, 1989	RR (b,d)
$(1.47 \pm 0.08) \times 10^{-12}$	298 ± 2	Nielsen et al., 1991	RR (b,e)

Comments

(a) Carried out at a total pressure of 1 bar Ar.

(b) HO radicals were generated by the photolysis of CH_3ONO in air at atmospheric pressure (0.97 bar to 1.0 bar). The concentrations of 1-butyl nitrate and the reference organic were measured by GC.

(c) The measured rate coefficient ratio of k(HO + 1-butyl nitrate)/k(HO + cyclohexane) = 0.187 ± 0.014 is placed on an absolute basis using k(HO + cyclohexane) = 7.00×10^{-12} cm^3 molecule^{-1} s^{-1} at 299 K (Atkinson, 2003). Experiments were carried out in an ~75 liter Teflon chamber, and the data were interpreted as involving concurrent photolysis of 1-butyl nitrate.

(d) Experiments were carried out in a 6400 liter Teflon chamber, and irradiations were also carried out in the absence of CH_3ONO, allowing the photolysis rate to be accurately allowed for in the data analysis. The measured rate coefficient ratio of k(HO + 1-butyl nitrate)/k(HO + cyclohexane) = 0.237 ± 0.025 is placed on an absolute basis using k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003). These data supersede those of Atkinson et al. (1982).

(e) The measured rate coefficient ratio k(HO + 1-butyl nitrate)/k(HO + 2-methylpropane) is placed on an absolute basis using k(HO + 2-methylpropane) = 2.12×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003).

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	1.6×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.06	298

Comments on Preferred Values

The absolute and relative rate coefficients of Atkinson and Aschmann (1989) (which supersedes the earlier data of Atkinson et al., 1982) and Nielsen et al. (1991) are in good agreement. The preferred value is an average of the absolute and relative rate constants of Atkinson and Aschmann (1989) and Nielsen et al., (1991). By analogy with the reaction of the HO radical with 2-propyl nitrate (IUPAC, 2019), the temperature dependence of the rate coefficient at temperatures below 300 K is likely to be small.

References

Atkinson, R.: Atmos. Chem. Phys. 3, 2233, 2003.
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Atkinson, R., Aschmann, S. M., Carter, W. P. L. and Winer, A. M.: Int. J. Chem. Kinet. 14, 919, 1982.
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Nielsen, O. J., Sidebottom, H. W., Donlon, M. and Treacy, J.: Chem. Phys. Lett. 178, 163, 1991.

HOx_VOC43: 2-butyl nitrate

Last evaluated: July 2007; Last change in preferred values: July 2007

$HO + 2\text{-}C_4H_9ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(6.4 \pm 1.0) \times 10^{-13}$	299 ± 2	Atkinson et al., 1982	RR (a,b)
$(8.6 \pm 1.5) \times 10^{-13}$	298 ± 2	Atkinson and Aschmann, 1989	RR (a,c)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of 2-butyl nitrate and the reference organic were measured by GC.

(b) Experiments were carried out in an ~75 liter Teflon chamber, and the data were interpreted as involving concurrent photolysis of 2-butyl nitrate. The measured rate constant ratio of k(HO + 2-butyl nitrate)/k(HO + cyclohexane) = 0.091 ± 0.013 is placed on an absolute basis using k(HO + cyclohexane) = 7.00×10^{-12} cm^3 molecule^{-1} s^{-1} at 299 K (Atkinson, 2003).

(c) Experiments were carried out in a 6400 liter Teflon chamber, and irradiations were also carried out in the absence of CH_3ONO allowing the loss of 2-butyl nitrate via photolysis rate to be measured and accounted for in the data analysis. The measured rate coefficient ratio of k(HO + 2-butyl nitrate)/k(HO + cyclohexane) = 0.123 ± 0.021 is placed on an absolute basis using k(HO + cyclohexane) = 6.97×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson, 2003). These data supersede those of Atkinson et al. (1982).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	8.6×10^{-13}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value is based on the rate coefficient of Atkinson and Aschmann (1989), which supersedes the earlier study of Atkinson et al. (1982). By analogy with the reaction of the HO radical with 2-propyl nitrate (IUPAC, 2019), the temperature dependence of the rate coefficient at temperatures below 300 K is likely to be small.

References

Atkinson, R.: Atmos. Chem. Phys. 3, 2233, 2003.

Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet. 21, 1123, 1989.

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HOx_VOC46: 1-nitrooxy-2-butanone

Last evaluated: August 2007; Last change in preferred values: August 2007

$HO + CH_3CH_2C(O)CH_2ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Technique/ Comments
Relative Rate Coefficients			
$(8.21 \pm 1.38) \times 10^{-13}$	298 ± 2	Zhu et al., 1991	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-N_2-O_2 mixtures at 1 bar pressure. The concentrations of $CH_3CH_2C(O)CH_2ONO_2$ and *n*-butane were measured during the experiments by GC, and the measured rate constant ratio of $k(HO + CH_3CH_2C(O)CH_2ONO_2)/k(HO + n\text{-butane}) = 0.357 \pm 0.060$ is placed on an absolute basis using $k(HO + n\text{-butane}) = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	8.2×10^{-13}	298
Reliability		
$\Delta \log k$	± 0.30	298

Comments on Preferred Values

The preferred value is based on the sole study of Zhu et al. (1991), but with a higher uncertainty.

References

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Zhu, T., Barnes, I. and Becker, K. H.: J. Atmos. Chem. 13, 301, 1991.

HOx_VOC47: 3-nitrooxy-2-butanone

Last evaluated: August 2007; Last change in preferred values: August 2007

$HO + CH_3CH(ONO_2)C(O)CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.15 \pm 0.13) \times 10^{-12}$	298 ± 2	Zhu et al., 1991	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-N_2-O_2 mixtures at 1 bar pressure. The concentrations of $CH_3CH(ONO_2)C(O)CH_3$ and *n*-butane were measured during the experiments by GC, and the measured rate constant ratio of $k(HO + CH_3CH(ONO_2)C(O)CH_3)/k(HO + n\text{-butane}) = 0.499 \pm 0.056$ is placed on an absolute basis using $k(HO + n\text{-butane}) = 2.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.2×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.30	298

Comments on Preferred Values

The preferred value is based on the sole study of Zhu et al. (1991), but with a higher uncertainty.

References

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Zhu, T., Barnes, I. and Becker, K. H.: J. Atmos. Chem. 13, 301, 1991.

HOx_VOC48: 2-methyl-1-(nitroperoxy)-2-propen-1-one (MPAN)

Last evaluated: August 2007; Last change in preferred values: August 2007

HO + $CH_2=C(CH_3)C(O)OONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(3.33 \pm 0.40) \times 10^{-12}$	298 ± 2	Grosjean et al., 1993	RR (a)
$(3.31 \pm 0.51) \times 10^{-11}$	275 ± 3	Orlando et al., 2002	RR (b,c)
$(2.94 \pm 0.46) \times 10^{-11}$	275 ± 3	Orlando et al., 2002	RR (b,d)

Comments

(a) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by the photolysis (using natural sunlight) of ethyl nitrite-air mixtures, and the concentrations of $CH_2=C(CH_3)C(O)OONO_2$ (MPAN) and 1-butyl nitrate (the reference compound) were measured by GC with electron capture detection. The measured rate coefficient ratio of k(HO + MPAN)/k(HO + 1-butyl nitrate) = 2.08 ± 0.25 is placed on an absolute basis using k(HO + 1-butyl nitrate) = 1.6×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

(b) Relative rate method carried out in synthetic air at 0.93-0.97 bar. HO radicals were generated by the photolysis of ethyl nitrite-NO-air mixtures, and the concentrations of $CH_2=C(CH_3)C(O)OONO_2$ (MPAN) and ethene and propene (the reference compounds) were measured by *in situ* FTIR spectroscopy. Experiments were carried out at 275 ± 3 K to decrease the rate of thermal decomposition of MPAN (IUPAC, 2019) in the presence of NO. The measured rate coefficient ratios of k(HO + MPAN)/k(HO + ethene) = 3.9 ± 0.6 and k(HO + MPAN)/k(HO + propene) = 0.95 ± 0.15 are placed on an absolute basis using rate coefficients at 275 K and atmospheric pressure of air of k(HO + ethene) = 8.48×10^{-12} cm^3 molecule^{-1} s^{-1} and k(HO + propene) = 3.1×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(c) Relative to HO + ethene.

(d) Relative to HO + propene.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.9×10^{-11}	298
Reliability		
$\Delta \log k$	$^{+0.2}_{-0.5}$	298

Comments on Preferred Values

The rate coefficients measured in the two studies of Grosjean et al. (1993) and Orlando et al. (2002) disagree by a factor of ≈10, for reasons which are not known. The reaction of HO radicals with $CH_2=C(CH_3)C(O)OONO_2$ is expected to proceed almost exclusively by initial

HO radical addition to the C=C bond (Grosjean et al., 1993; Orlando et al., 2002), and is expected to have a small (and probably negative) temperature dependence at around room temperature. Support for the Orlando et al. (2002) study arises from data for the structurally similar compound $CH_2=C(CH_3)C(O)OCH_3$ which has a rate coefficient for reaction with HO radicals of $(2.6 \pm 0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K (Saunders et al., 1994), which is similar to that measured by Orlando et al. (2002) for HO + MPAN. Accordingly, the preferred value is based on the rate coefficients measured by Orlando et al. (2002) at 275 K, adjusted to 298 K using the temperature dependence observed for HO + propene (IUPAC, 2019), and with appropriately large and asymmetric uncertainties. Formaldehyde and hydroxyacetone have been observed as products of this reaction (Grosjean et al., 1993; Orlando et al., 2002).

References

Grosjean, D., Williams II, E. L. and Grosjean, E.: Int. J. Chem. Kinet. 25, 921, 1993.
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Orlando, J. J., Tyndall, G. S., Bertman, S. B., Chen, W. and Burkholder, J. B.: Atmos. Environ. 36, 1895, 2002.
Saunders, S. M., Baulch, D. L., Cooke, K. M., Pilling, M. J. and Smurthwaite, P. I.: Int. J. Chem. Kinet. 26, 113, 1994.

HOx_VOC60: 2-methylpropane

Last evaluated: March 2009; Last change in preferred values: March 2009

$$\mathbf{HO + (CH_3)_3CH \rightarrow H_2O + (CH_3)_3C \quad (1)}$$
$$\mathbf{\rightarrow H_2O + (CH_3)_2CHCH_2 \quad (2)}$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.13 \pm 0.12) \times 10^{-12}$	297 ± 1	Greiner, 1967	FP-KS
$8.7 \times 10^{-12} \exp[-(387 \pm 63)/T]$	297-498	Greiner, 1970	FP-KS
$(2.67 \pm 0.17) \times 10^{-12}$	298		
$(2.70 \pm 0.20) \times 10^{-12}$	267	Trevor et al., 1982	PLP-RF
3.6×10^{-12}	298		
$(3.62 \pm 0.40) \times 10^{-12}$	324		
$(1.83 \pm 0.34) \times 10^{-12}$	296	Böhland et al., 1984	PLP-LMR
$(1.9 \pm 0.3) \times 10^{-12}$	295	Schmidt et al., 1985	PLP-LIF
$4.31 \times 10^{-17} T^{1.80} \exp(175/T)$	293-864	Tully et al., 1986a	PLP-LIF
$(2.19 \pm 0.11) \times 10^{-12}$	293		
$(2.09 \pm 0.42) \times 10^{-11}$	1146 ± 15	Bott and Cohen, 1989	SH-RA
$(2.11 \pm 0.09) \times 10^{-12}$	~298	Schiffman et al., 1991	PLP-IR
$9.32 \times 10^{-18} T^{2} \exp[(274 \pm 16)/T]$	231-372	Talukdar et al., 1994	PLP-LIF
$(2.10 \pm 0.16) \times 10^{-12}$	298		
$(2.09 \pm 0.06) \times 10^{-12}$	300	Donahue et al., 1998	DF-LIF
$(2.38 \pm 0.07) \times 10^{-12}$	325		
$(2.47 \pm 0.09) \times 10^{-12}$	340		
$(2.62 \pm 0.08) \times 10^{-12}$	375		
$(2.72 \pm 0.14) \times 10^{-12}$	390		
Relative Rate Coefficients			
1.9×10^{-11}	793	Baldwin and Walker, 1964	RR (a)
9.9×10^{-12}	753	Baker et al., 1970; Baldwin and Walker, 1979	RR (a)
$(3.43 \pm 0.86) \times 10^{12}$	298	Gorse and Volman, 1972/73, 1974	RR (b)
$(7.88 \pm 0.44) \times 10^{-12}$	653	Hucknall et al., 1975	RR (c)
2.2×10^{-12}	303	Wu et al., 1976	RR (d)
$(2.19 \pm 0.05) \times 10^{-12}$	300 ± 1	Darnall et al., 1978	RR (e)
$(2.06 \pm 0.05) \times 10^{-12}$	297 ± 2	Atkinson et al., 1984	RR (f)
$(2.17 \pm 0.31) \times 10^{-12}$	297.8 ± 0.4	Edney et al., 1986	RR (e)
$6.33 \times 10^{-21} T^{3.125} \exp(540/T)$	229-403	Wilson et al., 2006	RR (g)
2.09×10^{-12}	298		

Comments

(a) Derived from the effects of the addition of small amounts of 2-methylpropane to slowly reacting mixtures of $H_2 + O_2$. The loss of H_2 was followed by monitoring the pressure change due to the reaction $2H_2 + O_2 \rightarrow 2H_2O$, and the loss of 2-methylpropane was measured by GC. The rate coefficient ratios *k*(HO + 2-methylpropane)/*k*(HO + H_2) = 20 at 793 K (Baldwin and Walker, 1964) and 12.6 at 753 K (Baker et al., 1970; Baldwin and Walker, 1979) are placed on an absolute basis using *k*(HO + H_2) = 7.87 × 10^{-13} at 753 K and 9.62 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 793 K (Atkinson, 2003).

(b) HO radicals were generated by the photolysis of H_2O_2 at 254 nm in H_2O_2-CO-O_2-2-methylpropane mixtures at total pressures of 16-21 Torr (21-28 mbar) (Gorse and Volman, 1972/73). The effect of varying the 2-methylpropane concentration on the CO_2 production rate was investigated (Gorse and Volman, 1972/73), and a rate coefficient ratio of *k*(HO + 2-methylpropane)/*k*(HO + CO) = 23.5 derived (Gorse and Volman, 1974). This rate coefficient ratio is placed on an absolute basis using *k*(HO + CO) = 1.46 × 10^{-13} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019, using M = N_2).

(c) HO radicals were generated by the decomposition of H_2O_2 in a boric acid-coated reaction vessel, and the concentrations of 2-methylpropane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios of *k*(HO + 2-methylpropane)/*k*(HO + propane) = 1.28 ± 0.07 is placed on an absolute value using *k*(HO + propane) = 6.16 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 653 K (IUPAC, 2019).

(d) HO radicals were generated by the photolysis of organic-NO_x-O_2-air mixtures at atmospheric pressure. 2-Methylpropane and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio *k*(HO + 2-methylpropane)/*k*(HO + *cis*-2-butene) = 0.04 is placed on an absolute basis using *k*(HO + *cis*-2-butene) = 5.45 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 303 K (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of 2-methylpropane and *n*-butane (the reference compound) were measured by GC. The measured rate coefficient ratios *k*(HO + 2-methylpropane)/*k*(HO + *n*-butane) are placed on an absolute basis by using *k*(HO + *n*-butane) = 2.34 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K and 2.37 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 300 K (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of 2-methylpropane and *n*-butane (the reference compound) were measured by GC. The measured rate coefficient ratio *k*(HO + 2-methylpropane)/*k*(HO + *n*-butane) = 0.886 ± 0.021 is placed on an absolute basis using *k*(HO + *n*-butane) = 2.33 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 297 K (IUPAC, 2019).

(g) HO radicals were generated by the photolysis of H_2O at 185 nm or, at low temperatures, by the photolysis of N_2O at 185 nm in the presence of H_2. The concentrations of 2-methylpropane and *n*-butane (the reference compound) were measured by GC/MS. The measured rate coefficient ratios *k*(HO + 2-methylpropane)/*k*(HO + *n*-butane) are placed on an absolute basis using *k*(HO + *n*-butane) = 2.03 × 10^{-17} T^2 exp(78/*T*) cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 $molecule^{-1}$ s^{-1}	2.1 × 10^{-12}	298
k /cm^3 $molecule^{-1}$ s^{-1}	5.4 × 10^{-12} exp(-285/*T*)	210-300
Reliability		
Δ log *k*	± 0.04	298
Δ E/R	± 150	210-300

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients of Tully et al. (1986a), Bott and Cohen (1989), Talukdar et al. (1994) and Donahue et al. (1998) and the relative rate coefficients of Baker et al. (1970) [as re-evaluated by Baldwin and Walker (1979)], Hucknall et al. (1975), Atkinson et al. (1984) [which is taken to supersede the earlier study of Darnall et al. (1978)] and Wilson et al. (2006). The three parameter expression, $k = CT^2 \exp(-D/T)$, was fitted to the rate coefficients from these studies, resulting in $k = 1.17 \times 10^{-17}\ T^2 \exp(213/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 210-1150 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 250 K and is derived from the three parameter expression with $A = C\, e^2\, T^2$ and $B = D + 2T$. The preferred values are in good agreement with the room temperature absolute and relative rate coefficients of Greiner (1967, 1970), Böhland et al. (1984), Schmidt et al. (1985), Schiffman et al. (1991), Wu et al. (1976), Darnall et al. (1978) and Edney et al. (1986), which were not used in the evaluation of the rate coefficient.

Tully et al. (1986a) also measured rate coefficients for the reaction of the HO radical with 2-methylpropane-d$_1$, 2-methylpropane-d$_9$ and 2-methylpropane-d$_{10}$. Combining their rate coefficients for 2-methylpropane, 2-methylpropane-d$_1$, 2-methylpropane-d$_9$ and 2-methylpropane-d$_{10}$ with the deuterium isotope ratio k_H/k_D for -CH$_3$/-CD$_3$ groups obtained from the 2,2-dimethylpropane (neopentane) reaction (Tully et al., 1985, 1986b), Tully et al. (1986a) derived rate coefficients for H-atom abstraction from the primary C-H bonds of the three CH$_3$ groups ($3k_{\text{primary}}$) and from the tertiary C-H bond in the CH group (k_{tertiary}), of $3k_{\text{primary}} = 3.81 \times 10^{-16}\ T^{1.53} \exp(-391/T)$ cm^3 molecule^{-1} s^{-1} (6.3×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K) and $k_{\text{tertiary}} = 9.52 \times 10^{-14}\ T^{0.51} \exp(-32/T)$ cm^3 molecule^{-1} s^{-1} (1.56×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K).

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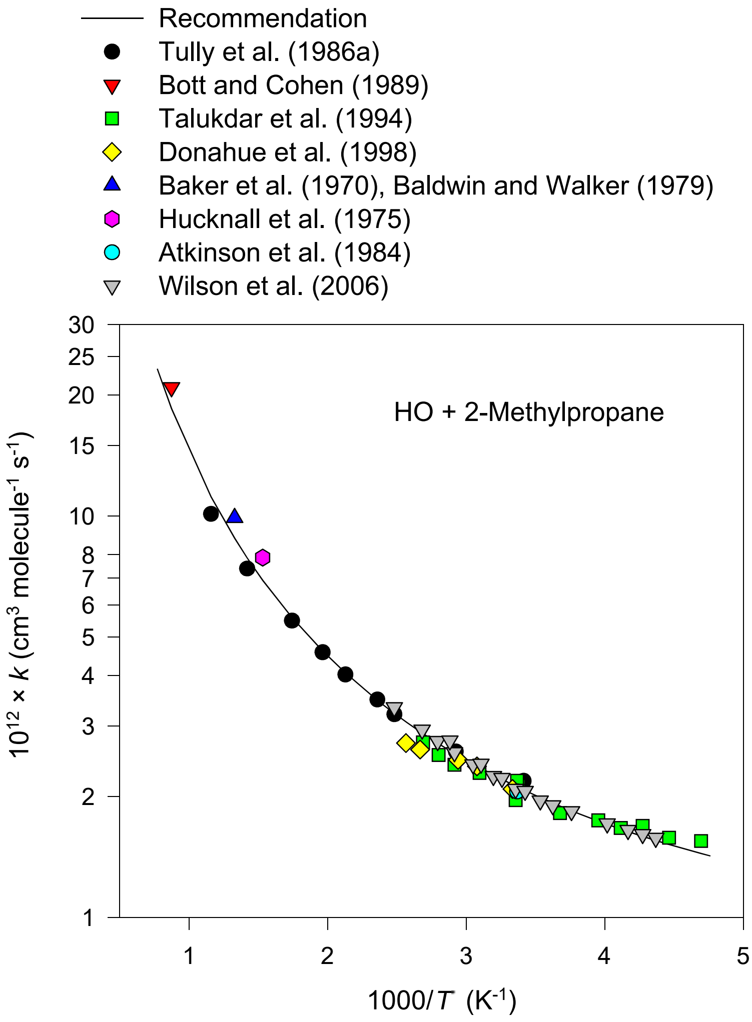

Rate coefficients for HO + 2-methylpropane.

HOx_VOC61: 2-methylpropene

Last evaluated: March 2009; Last change in preferred values: March 2009

HO + $(CH_3)_2C=CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$9.2 \times 10^{-12} \exp[(503 \pm 151)/T]$	297-424	Atkinson and Pitts, 1975	FP-RF (a)
$(5.07 \pm 0.51) \times 10^{-11}$	297.2		
Relative Rate Coefficients			
6.46×10^{-11}	298	Morris and Niki, 1971a	DF-MS (b)
5.01×10^{-11}	303	Wu et al., 1976	RR (c)
5.68×10^{-11}	300	Barnes et al., 1982	RR (d)
$(5.47 \pm 0.09) \times 10^{-11}$	298 ± 2	Ohta, 1984	RR (e)
$(5.64 \pm 0.25) \times 10^{-11}$	295 ± 1	Atkinson and Aschmann, 1984	RR (f)

Comments

(a) Experiments carried out at 25 Torr (33 mbar) of Ar diluent.

(b) A rate coefficient for HO + 2-methylpropene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of 2-methylpropene and propene and the average HO radical concentrations under identical experimental conditions. The rate coefficient ratio k(HO + 2-methylpropene)/k(HO + propene) = 3.8 is placed on an absolute basis using k(HO + propene) = 1.7×10^{-11} cm^3 molecule^{-1} s^{-1} under the experimental condition used (Morris and Niki, 1971b).

(c) HO radicals were generated by the photolysis of organic-NO_x-O_2-air mixtures at atmospheric pressure. 2-Methylpropene and *cis*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio k(HO + 2-methylpropene)/k(HO + *cis*-2-butene) = 0.92 is placed on an absolute basis using k(HO + *cis*-2-butane) = 5.45×10^{-11} cm^3 molecule^{-1} s^{-1} at 303 K (IUPAC, 2019).

(d) HO radicals were generated by decomposition of $HOONO_2$ in the dark in the presence of NO at atmospheric pressure of N_2 or air. 2-Methylpropene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + 2-methylpropene)/k(HO + ethene) = 7.3 is placed on an absolute basis using a rate coefficient of k(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of H_2O_2 at 253.7 nm in 760 Torr (1013 mbar) of N_2 or O_2 diluent in a quartz vessel. The concentrations of 2-methylpropene and 2-methyl-2-butene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratios k(HO + 2-methylpropene)/k(HO + 2-methyl-2-butene) = 0.63 ± 0.01 is placed on an absolute basis using k(HO + 2-methyl-2-butene) = 8.69×10^{-11} at 298 K and atmospheric pressure of air (Atkinson and Arey, 2003).

(f) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a ~60 L Teflon chamber at atmospheric pressure of air. The concentrations of 2-methylpropene and propene (the reference compound) were monitored by GC during the experiments. The measured rate coefficient ratio k(HO + 2-methylpropene)/k(HO + propene)

= 1.95 ± 0.09 is placed on an absolute basis using k(HO + propene) = 2.89 × 10^{-11} cm^3 molecule^{-1} s^{-1} at 295 K and atmospheric pressure of air (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	5.1×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$9.4 \times 10^{-12} \exp(505/T)$	290-430
Reliability		
$\Delta \log k$	± 0.04	298
Δ E/R	± 200	290-430

Comments on Preferred Values

At room temperature, the absolute rate coefficient of Atkinson and Pitts (1975) and the relative rate coefficients of Wu et al. (1976), Barnes et al. (1982), Ohta (1984) and Atkinson and Aschmann (1984) are in reasonable agreement. Using propene as the reference compound, Atkinson and Aschmann (1984) measured rate coefficients for 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, propadiene, 1,3-butadiene and isoprene at 295 ± 1 K and atmospheric pressure of air. These relative rate data were fit by Atkinson (1989) to the absolute rate coefficients then available for propene, 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, propadiene and 1,3-butadiene (Atkinson and Pitts, 1975, 1978; Atkinson et al., 1977; Ravishankara et al., 1978; Nip and Paraskevopoulos, 1979; Tully and Goldsmith, 1985), using the observed temperature dependencies or E/R = -500 K to adjust the measured rate coefficients to 295 K. The result of this fitting procedure (Atkinson, 1989) was that for 2-methylpropene, $k = 5.23 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 295 K. Combined with the temperature dependence of Atkinson and Pitts (1975), this leads to the preferred values.

At room temperature and below, the reaction proceeds dominantly by HO radical addition to the C=C bond. At elevated temperatures (>650 K), the HO-2-methylpropene adducts decompose rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

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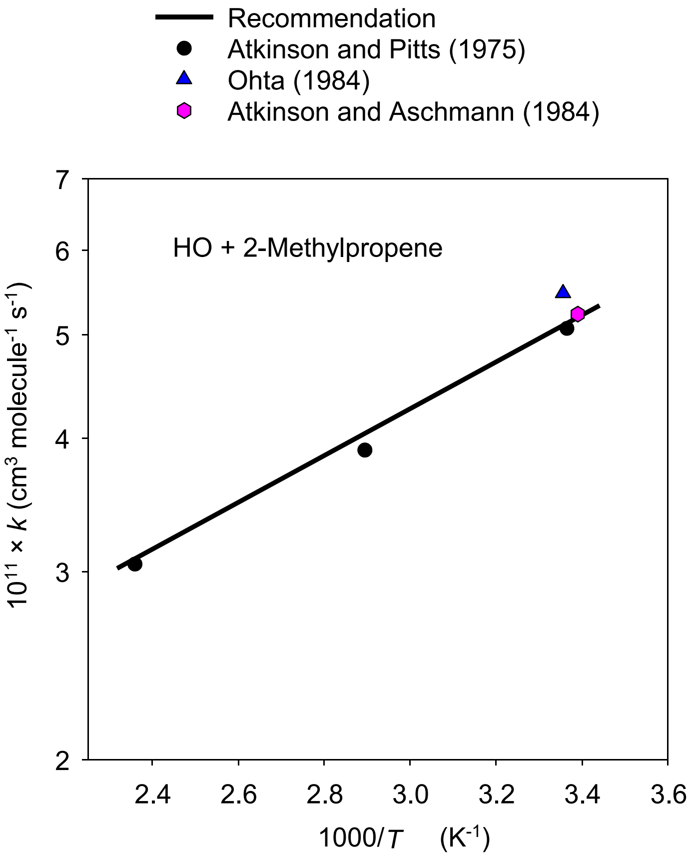

Rate coefficients for HO + 2-methylpropene.

HOx_VOC62: 1-butene

Last evaluated: March 2009; Last change in preferred values: March 2009

$HO + CH_3CH_2CH{=}CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.5 \pm 0.1) \times 10^{-11}$	300	Pastrana and Carr, 1975	DF-RF (a)
$7.6 \times 10^{-12} \exp[(468 \pm 151)/T]$	298-424	Atkinson and Pitts, 1975	FP-RF (b)
$(3.53 \pm 0.36) \times 10^{-11}$	297.7		
$(2.94 \pm 0.14) \times 10^{-11}$	298	Ravishankara et al., 1978	FP-RF (c)
$(3.34 \pm 0.25) \times 10^{-11}$	297 ± 2	Nip and Paraskevopoulos, 1979	FP-RA (d)
$(3.0 \pm 0.4) \times 10^{-11}$	298	Biermann et al., 1982	DF-MS (e)
1.6×10^{-11}	478	Liu et al., 1989	PR-RA (f)
$(7.71 \pm 1.06) \times 10^{-11}$	170	Sims et al., 1994	PLP-LIF (g)
$(3.49 \pm 0.11) \times 10^{-11}$	295		
$(3.30 \pm 0.12) \times 10^{-11}$	295		
$(5.80 \pm 1.51) \times 10^{-11}$	165 ± 14	Vakhtin et al., 2001, 2003	PLP-LIF (h)
$(8.13 \pm 2.10) \times 10^{-11}$	165 ± 14		
$(3.0 \pm 0.2) \times 10^{-11}$	296 ± 2		
Relative Rate Coefficients			
4.08×10^{-11}	298	Morris and Niki, 1971a	DF-MS (i)
2.83×10^{-11}	303	Wu et al., 1976	RR (j)
2.96×10^{-11}	300	Barnes et al., 1982	RR (k)
$(3.40 \pm 0.08) \times 10^{-11}$	298 ± 2	Ohta, 1984	RR (l)
$(3.44 \pm 0.17) \times 10^{-11}$	295 ± 1	Atkinson and Aschmann, 1984	RR (m)

Comments

(a) Experiments carried out at 1 Torr (1.3 mbar) of He diluent.

(b) Experiments carried out at 25 Torr (33 mbar) of Ar diluent.

(c) Rate coefficients measured at 3 and 20 Torr (4 and 27 mbar) of helium diluent, with rate coefficients of $(2.96 \pm 0.19) \times 10^{-11}$ and $(2.94 \pm 0.14) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. Value cited in the table is that at 20 Torr (26.7 mbar) He.

(d) Experiments carried out at 55 Torr (73 mbar) of (91% H_2 + 9% N_2O) diluent.

(e) 1-Butene was in ~10-fold excess of HO radical; concentrations, and the concentrations of 1-butene were monitored by photoionization mass spectrometry at m/z = 56. Experiments were carried out at ~2 Torr (~2.7 mbar) of He.

(f) Rate coefficients measured over the temperature range 478-853 K at 760 Torr (1.013 bar) of Ar diluent. Data were presented graphically and not tabulated.

(g) Experiments at 295 K were carried out at total pressures of Ar diluent of 14 and 23 Torr (19 and 31 mbar), with respective rate coefficients of $(3.49 \pm 0.11) \times 10^{-11}$ and $(3.30 \pm 0.12) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Rate coefficients of $(4.27 \pm 0.56) \times 10^{-10}$, $(3.15 \pm 0.40) \times 10^{-10}$ and $(2.73 \pm 0.16) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} were also measured at 23, 44 and 75 K, respectively.

(h) Rate coefficients of $(1.74 \pm 0.28) \times 10^{-10}$, $(1.24 \pm 0.27) \times 10^{-10}$ and $(1.68 \pm 0.40) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} were also measured at 96 ± 4, 103 ± 9 and 110 ± 7 K, respectively. The rate coefficient cited in the table for 296 ± 2 K is an average value of five measurements made over the pressure range 0.88-102 Torr (1.2-136 mbar) of N_2 diluent gas; no pressure dependence was observed over this pressure range.

(i) A rate coefficient for HO + 1-butene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of 1-butene and propene and the respective average HO radical concentrations under identical experimental conditions. The rate coefficient ratio k(HO + 1-butene)/k(HO + propene) = 2.4 is placed on an absolute basis using k(HO + propene) = 1.7×10^{-11} cm^3 $molecule^{-1}$ s^{-1} under the experimental condition used (Morris and Niki, 1971b).

(j) HO radicals were generated by the photolysis of organic-NO_x-O_2-air mixtures at atmospheric pressure. 1-Butene and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio k(HO + 1-butene)/k(HO + *cis*-2-butene) = 0.52 is placed on an absolute basis using k(HO + *cis*-2-butane) = 5.45×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 303 K (IUPAC, 2019).

(k) HO radicals were generated by dark decomposition of $HOONO_2$ in the presence of NO at atmospheric pressure of N_2 or air. 1-Butene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + 1-butene)/k(HO + ethene) = 3.8 is placed on an absolute basis using a rate coefficient of k(HO + ethene) = 7.78×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 300 K and atmospheric pressure of air (IUPAC, 2019).

(l) HO radicals were generated by the photolysis of H_2O_2 at 253.7 nm in 760 Torr (1013 mbar) of N_2 or O_2 diluent in a quartz vessel. The concentrations of 1-butene and propene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratios k(HO + propene)/k(HO + 1-butene) = 0.84 ± 0.02 is placed on an absolute basis using k(HO + propene) = 2.86×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K and atmospheric pressure of air (IUPAC, 2019).

(m) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a ~60 L Teflon chamber at atmospheric pressure of air. The concentrations of 1-butene and propene (the reference compound) were monitored by GC during the experiments. The measured rate coefficient ratio k(HO + 1-butene)/k(HO + propene) = 1.19 ± 0.06 is placed on an absolute basis using k(HO + propene) = 2.89×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 295 K and atmospheric pressure of air (IUPAC, 2019).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 $molecule^{-1}$ s^{-1}	3.1×10^{-11}	298
k /cm^3 $molecule^{-1}$ s^{-1}	$6.6 \times 10^{-12} \exp(465/T)$	290-430
Reliability		
$\Delta \log k$	± 0.06	298
Δ E/R	± 150	290-430

Comments on Preferred Values

At room temperature, the absolute rate coefficients of Atkinson and Pitts (1975), Ravishankara et al. (1978), Biermann et al. (1982), Sims et al. (1994) and Vakhtin et al. (2001, 2003) and the relative rate coefficients of Wu et al. (1976), Barnes et al. (1982), Ohta (1984) and Atkinson and Aschmann (1984) are in reasonable agreement, with the relative rate studies of Ohta

(1984) and Atkinson and Aschmann (1984) obtaining identical rate coefficient ratios of *k*(HO + 1-butene)/*k*(HO + propene) = 1.19 ± 0.03 at 298 ± 2 K and 1.19 ± 0.06 at 295 ± 1 K, respectively. Using propene as the reference compound, Atkinson and Aschmann (1984) measured rate coefficients for 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, propadiene, 1,3-butadiene and isoprene at 295 ± 1 K and atmospheric pressure of air. These relative rate data for were fit by Atkinson (1989) to the absolute rate coefficients then available for propene, 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, propadiene and 1,3-butadiene (Atkinson and Pitts, 1975, 1978; Atkinson et al., 1977; Ravishankara et al., 1978; Nip and Paraskevopoulos, 1979; Tully and Goldsmith, 1985), using the observed temperature dependencies or E/R = -500 K to adjust the measured rate coefficients to 295 K. The result of this fitting procedure (Atkinson, 1989) was that for 1-butene, $k = 3.19 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 295 K. Combined with the temperature dependence of Atkinson and Pitts (1975), this leads to the preferred values.

The more recent absolute rate coefficients of Sims et al. (1994) and Vakhtin et al. (2001, 2003) at 295-296 K are in good agreement with the preferred value, and the 478 K rate coefficient of Liu et al. (1989) is in good agreement with extrapolation of the recommended rate expression. The preferred Arrhenius expression should not be used much below room temperature; clearly extrapolation to 165-170 K leads to overprediction of the measured rate coefficients of Sims et al. (1994) and Vakhtin et al. (2001, 2003). Rather, the expression of the form $k = a \exp(-bT)$ appears to give a reasonable fit, with $a = 2.56 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $b = 0.00705$ (Atkinson and Arey, 2003).

At room temperature and below, the reaction proceeds by HO radical addition to the C=C bond, with H-atom abstraction accounting for <10% of the overall reaction at room temperature (Atkinson et al., 1985). At elevated temperatures (>650 K), the HO-1-butene adducts decompose rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

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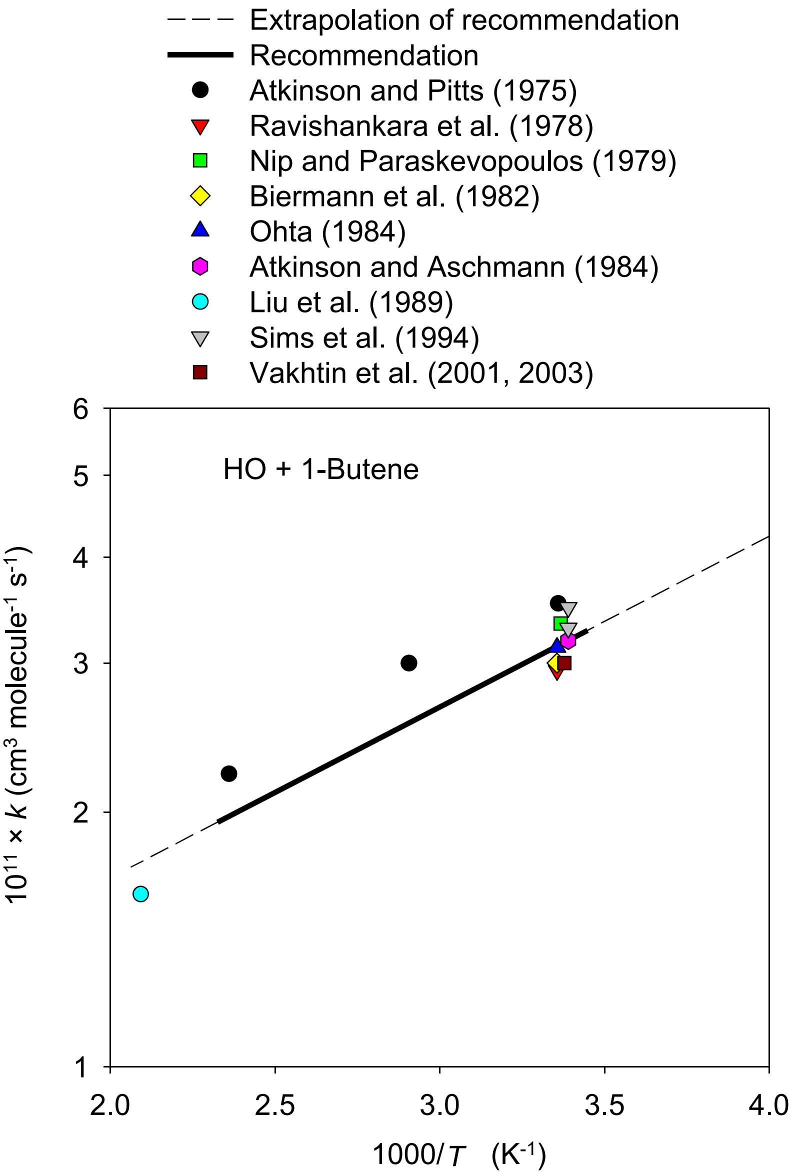
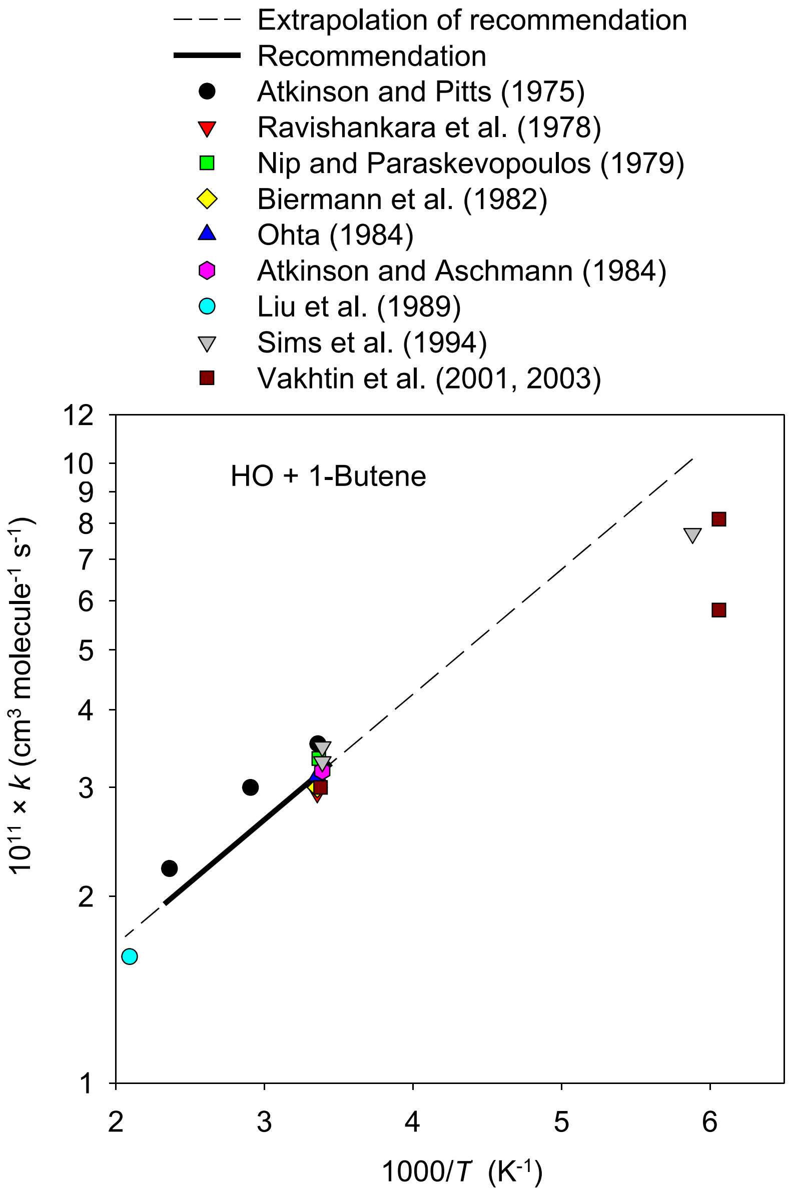


Rate coefficients for HO + 1-butene.



Rate coefficients for HO + 1-butene.

HOx_VOC63: *cis*-2-butene

Last evaluated: March 2009; Last change in preferred values: March 2009

HO + *cis*-$CH_3CH{=}CHCH_3$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$1.04 \times 10^{-11} \exp[(488 \pm 151)/T]$	298-425	Atkinson and Pitts, 1975	FP-RF (a)
$(5.37 \pm 0.54) \times 10^{-11}$	297.6		
$(4.26 \pm 0.25) \times 10^{-11}$	298	Ravishankara et al., 1978	FP-RF (b)
$(1.30 \pm 0.13) \times 10^{-10}$	170	Sims et al., 1994	PLP-LIF (c)
$(6.18 \pm 0.57) \times 10^{-11}$	295		
Relative Rate Coefficients			
6.12×10^{-11}	298	Morris and Niki, 1971a	DF-MS (d)
$(5.3 \pm 1.1) \times 10^{-11}$	305 ± 2	Lloyd et al., 1976	RR (e)
$(6.0 \pm 1.2) \times 10^{-11}$	305 ± 2	Winer et al., 1976	RR (f)
$(5.47 \pm 0.18) \times 10^{-11}$	298 ± 2	Ohta, 1984	RR (g)
$(6.16 \pm 0.14) \times 10^{-11}$	295 ± 1	Atkinson and Aschmann, 1984	RR (h)

Comments

(a) Experiments carried out at 25 Torr (33 mbar) of Ar.

(b) Rate coefficients measured at 3 and 20 Torr (4 and 27 mbar) of helium diluent, with rate coefficients of $(4.32 \pm 0.41) \times 10^{-11}$ and $(4.26 \pm 0.25) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. Value cited in the table is that at 20 Torr He.

(c) Experiments at 295 K were carried out at a total pressure of Ar diluent of 14 Torr (19 mbar). Rate coefficients of $(3.89 \pm 0.23) \times 10^{-10}$, $(3.28 \pm 0.33) \times 10^{-10}$ and $(3.02 \pm 0.14) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} were also measured at 23, 44 and 75 K, respectively.

(d) A rate coefficient for HO + *cis*-2-butene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of *cis*-2-butene and propene and the respective average HO radical concentrations under identical experimental conditions. The rate coefficient ratio k(HO + *cis*-2-butene)/k(HO + propene) = 3.6 is placed on an absolute basis using k(HO + propene) = 1.7×10^{-11} cm^3 molecule^{-1} s^{-1} (Morris and Niki, 1971b).

(e) HO radicals generated by the photolysis of organic-NO_x mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of *cis*-2-butene and *n*-butane (the reference compound) by GC. The measured rate coefficient ratio k(HO + *cis*-2-butene)/k(HO + *n*-butane) = 21.8 ± 4.4 is placed on an absolute basis using k(HO + *n*-butane) = 2.44×10^{-12} cm^3 molecule^{-1} s^{-1} at 305 K (IUPAC, 2019).

(f) HO radicals generated by the photolysis of organic-NO_x mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of *cis*-2-butene and 2-methylpropene (the reference compound) by GC. The measured rate coefficient ratio k(HO + *cis*-2-butene)/k(HO + 2-methylpropene) = 1.22 ± 0.25 is placed on an absolute basis using k(HO + 2-methylpropene) = 4.92×10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (IUPAC, 2019).

(g) HO radicals were generated by the photolysis of H_2O_2 at 253.7 nm in 760 Torr (1013 mbar) of N_2 or O_2 diluent in a quartz vessel. The concentrations of *cis*-2-butene and 2-methyl-2-butene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratio k(HO + *cis*-2-butene)/k(HO + 2-methyl-2-butene) = 0.63 ± 0.02 is placed on an absolute basis using k(HO + 2-methyl-2-butene) = 8.69 × 10^{-11} at 298 K and atmospheric pressure of air (Atkinson and Arey, 2003).

(h) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a ~60 L Teflon chamber at atmospheric pressure of air. The concentrations of 1-butene and propene (the reference compound) were monitored by GC during the experiments. The measured rate coefficient ratio k(HO + *cis*-2-butene)/k(HO + propene) = 2.13 ± 0.05 is placed on an absolute basis using k(HO + propene) = 2.89 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 295 K and atmospheric pressure of air (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	5.6 × 10^{-11}	298
k /cm^3 $molecule^{-1}$ s^{-1}	1.1 × 10^{-11} exp(485/T)	290-430
Reliability		
Δ log k	± 0.10	298
Δ E/R	± 200	290-430

Comments on Preferred Values

At room temperature, the absolute rate coefficients of Atkinson and Pitts (1975) and Sims et al. (1994) and the relative rate coefficients of Lloyd et al. (1976), Winer et al. (1976), Ohta (1984) and Atkinson and Aschmann (1984) are in reasonable agreement, with those of Lloyd et al. (1976) and Winer et al. (1976) having large associated uncertainties. The absolute rate coefficient of Ravishankara et al. (1978) is ~20% lower, possibly because of wall losses of *cis*-2-butene in the static reaction vessel used (Atkinson, 1989). Using propene as the reference compound, Atkinson and Aschmann (1984) measured rate coefficients for 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, propadiene, 1,3-butadiene and isoprene at 295 ± 1 K and atmospheric pressure of air. These relative rate data were fit by Atkinson (1989) to the absolute rate coefficients then available for propene, 1-butene, 3-methyl-1-butene, 2-methylpropene, *cis*-2-butene, *trans*-2-butene, 2-methyl-2-butene, propadiene and 1,3-butadiene (Atkinson and Pitts, 1975, 1978; Atkinson et al., 1977; Ravishankara et al., 1978; Nip and Paraskevopoulos, 1979; Tully and Goldsmith, 1985), using the observed temperature dependencies or E/R = -500 K to adjust the measured rate coefficients to 295 K. The result of this fitting procedure (Atkinson, 1989) was that for *cis*-2-butene, k = 5.71 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 295 K. Combined with the temperature dependence of Atkinson and Pitts (1975), this leads to the preferred values.

The more recent absolute rate coefficient of Sims et al. (1994) at 295 K is in agreement with the preferred value within the experimental uncertainties. The preferred Arrhenius expression should not be used much below room temperature; clearly extrapolation to 170 K leads to overprediction of the measured rate coefficient of Sims et al. (1994). Rather, the expression of the form $k = a \exp(-bT)$ appears to give a reasonable fit, with a = 4.0 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} and b = 0.0066, based on the preferred 295 K rate coefficient and the 170 K rate coefficient of Sims et al. (1994).

At room temperature and below, the reaction proceeds by HO radical addition to the C=C bond. At elevated temperatures (>650 K), the HO-*cis*-2-butene adduct is expected to decompose rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

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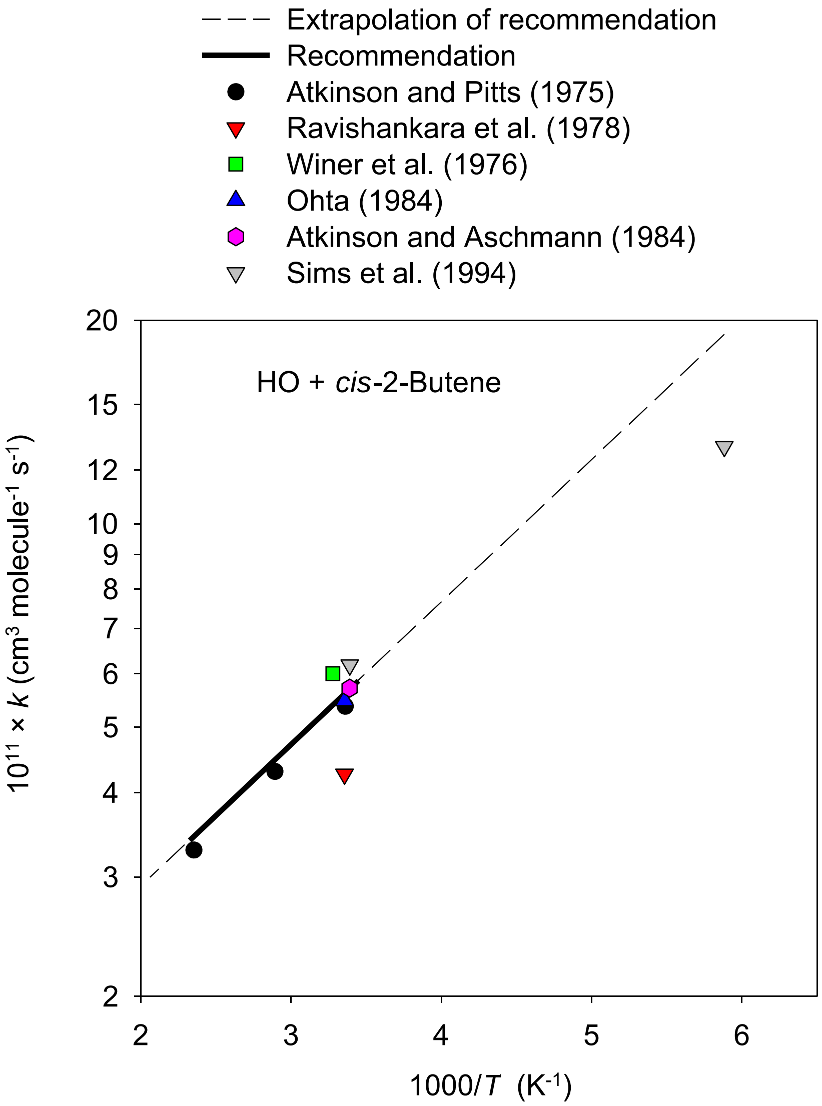
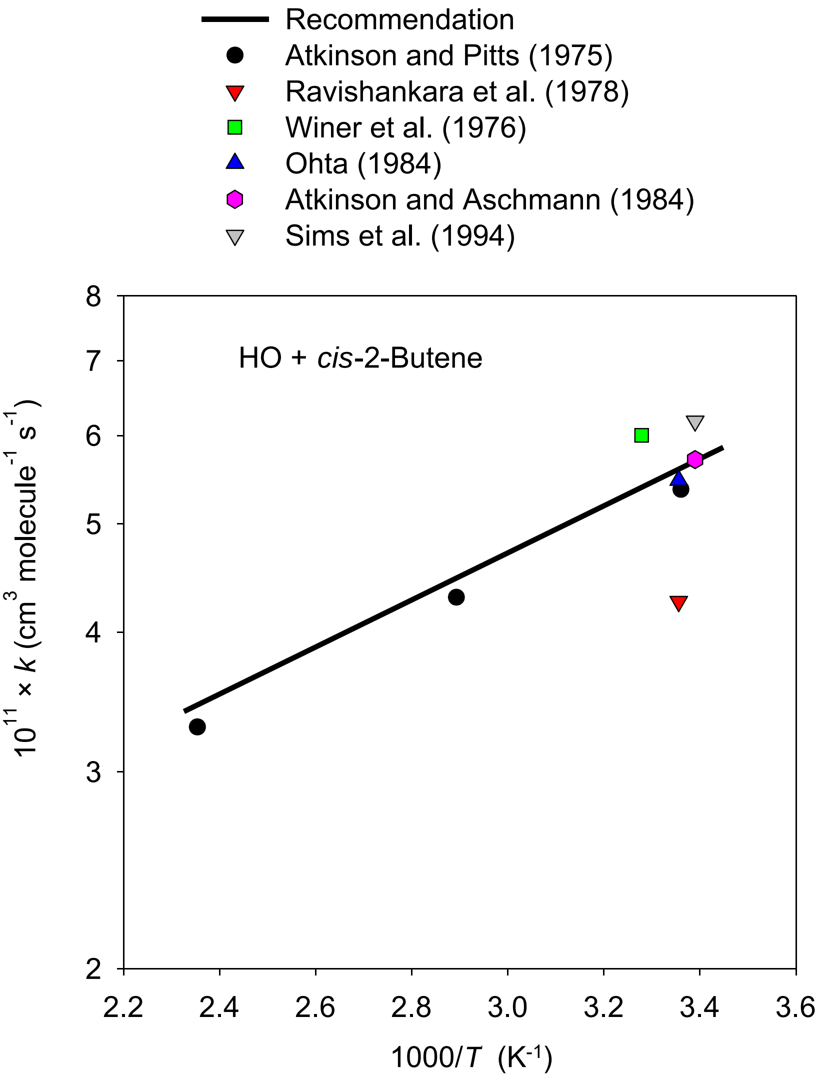


Rate coefficients for HO + *cis*-2-butene.



Rate coefficients for HO + cis-2-butene.

HOx_VOC64: *trans*-2-butene

Last evaluated: March 2009; Last change in preferred values: March 2009

HO + *trans*-$CH_3CH=CHCH_3$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.2 \pm 1) \times 10^{-11}$	300	Pastrana and Carr, 1975	DF-RA (a)
$1.12 \times 10^{-11} \exp[(549 \pm 151)/T]$	298-425	Atkinson and Pitts, 1975	FP-RF (b)
$(6.99 \pm 0.70) \times 10^{-11}$	297.8		
$(1.69 \pm 0.083) \times 10^{-10}$	170	Sims et al., 1994	PLP-LIF (c)
$(6.83 \pm 0.22) \times 10^{-11}$	295		
Relative Rate Coefficients			
12.0×10^{-11}	298	Morris and Niki, 1971	DF-MS (d)
7.09×10^{-11}	303	Wu et al., 1976	RR (e)
$(5.96 \pm 0.31) \times 10^{-11}$	298 ± 2	Ohta, 1983	RR (f)
$(7.02 \pm 0.14) \times 10^{-11}$	295 ± 1	Atkinson and Aschmann, 1984	RR (g)
$(7.9 \pm 1.3) \times 10^{-11}$	297.4 ± 1.7	Edney et al., 1986	RR (h)
$(7.87 \pm 0.38) \times 10^{-11}$	298 ± 3	Rogers, 1989	RR (i)

Comments

(a) Experiments carried out at 1 Torr (1.3 mbar) of He.

(b) Experiments carried out at 25 Torr (33 mbar) of Ar.

(c) Experiments at 295 K were carried out at a total pressure of Ar diluent of 14 Torr (19 mbar). Rate coefficients of $(4.52 \pm 0.32) \times 10^{-10}$, $(4.03 \pm 0.44) \times 10^{-10}$ and $(3.17 \pm 0.24) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} were also measured at 23, 44 and 75 K, respectively.

(d) A rate coefficient for HO + *trans*-2-butene was obtained relative to that for propene at 1 Torr (1.3 mbar) He diluent by monitoring the decays of *trans*-2-butene and propene and the average HO radical concentrations under identical experimental conditions. The measured rate coefficient ratio k(HO + *trans*-2-butene)/k(HO + propene) = 4.2 is placed on an absolute basis using k(HO + propene) = 1.86×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of organic-NO_x-O_2-air mixtures at atmospheric pressure. *trans*-2-Butene and *cis*-2-butene (the reference compound) were measured by GC, and the measured rate coefficient ratio k(HO + *trans*-2-butene)/k(HO + *cis*-2-butene) = 1.3 is placed on an absolute basis using k(HO + *cis*-2-butene) = 5.45×10^{-11} cm^3 molecule^{-1} s^{-1} at 303 K (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of H_2O_2 at 253.7 nm in 760 Torr (1013 mbar) of N_2 or O_2 diluent in a quartz vessel. The concentrations of *trans*-2-butene and *cis*-1,3-pentadiene (the reference compound) were measured by GC during the experiments. The measured rate coefficient ratios k(HO + *trans*-2-butene)/k(HO + *cis*-1,3-pentadiene) = 0.59 ± 0.03 is placed on an absolute basis using k(HO + *cis*-1,3-pentadiene) = 1.01×10^{-10} at 298 K and atmospheric pressure of air (Atkinson, 1989; Atkinson and Arey, 2003).

(g) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a ~60 L Teflon chamber at atmospheric pressure of air. The concentrations of *trans*-2-butene and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + *trans*-2-butene)/k(HO + propene) = 2.43 ± 0.05 is placed on an absolute basis using k(HO + propene) = 2.89 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 295 K and atmospheric pressure of air (IUPAC, 2019).

(h) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of *trans*-2-butene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of k(HO + *trans*-2-butene)/k(HO + propene) is placed on an absolute basis using a rate coefficient at 297 K and atmospheric pressure of air of k(HO + propene) = 2.86 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

(i) HO radicals were generated by the photolysis of HONO in one atmosphere of air in a 600 L stainless steel cell. The concentrations of *trans*-2-butene and propene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio k(HO + propene)/k(HO + *trans*-2-butene) = 0.365 ± 0.019 is placed on an absolute basis using rate coefficients at 298 K and atmospheric pressure of air of k(HO + propene) = 2.87 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	7.1 × 10^{-11}	298
k /cm^3 $molecule^{-1}$ s^{-1}	1.1 × 10^{-11} exp(553/T)	290-430
Reliability		
Δ log k	± 0.06	298
Δ E/R	± 200	290-430

Comments on Preferred Values

At room temperature, the absolute rate coefficients of Atkinson and Pitts (1975), and Sims et al. (1994) and the relative rate coefficients of Wu et al. (1976), Ohta (1983), Atkinson and Aschmann (1984), Edney et al. (1986) and Rogers (1989) are in reasonable agreement, with that of Edney et al. (1986) having a large associated uncertainty. The preferred value is based on the relative studies and the absolute ones from Sims et al. (1994) at 295 K and Atkinson and Pitts (1975).

The preferred Arrhenius expression should not be used much below room temperature; clearly extrapolation to 170 K leads to overprediction of the measured rate coefficient of Sims et al. (1994). Rather, the expression of the form $k = a \exp(-bT)$ appears to give a reasonable fit, with $a = 6.1 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} and $b = 0.0076$, based on the preferred 295 K value and the 170 K rate coefficient of Sims et al. (1994).

At room temperature and below, the reaction proceeds by HO radical addition to the C=C bond. At elevated temperatures (>650 K), the HO-*trans*-2-butene adduct decomposes rapidly back to reactants and the observed reaction is then H-atom abstraction (Atkinson, 1989).

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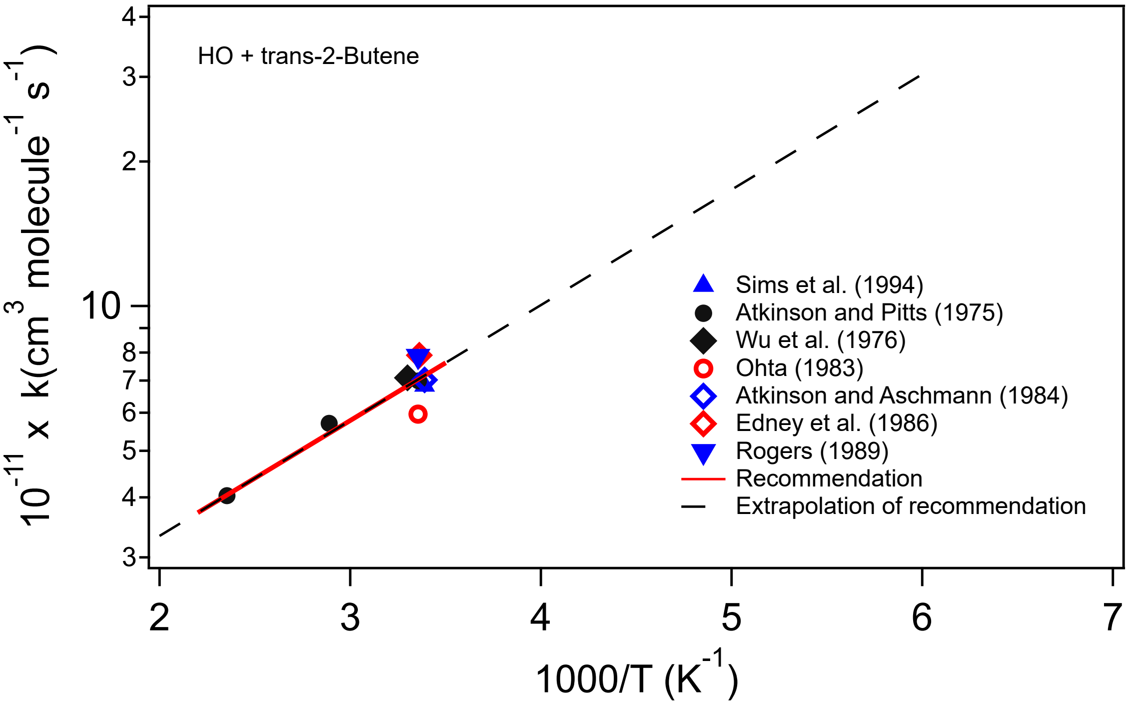

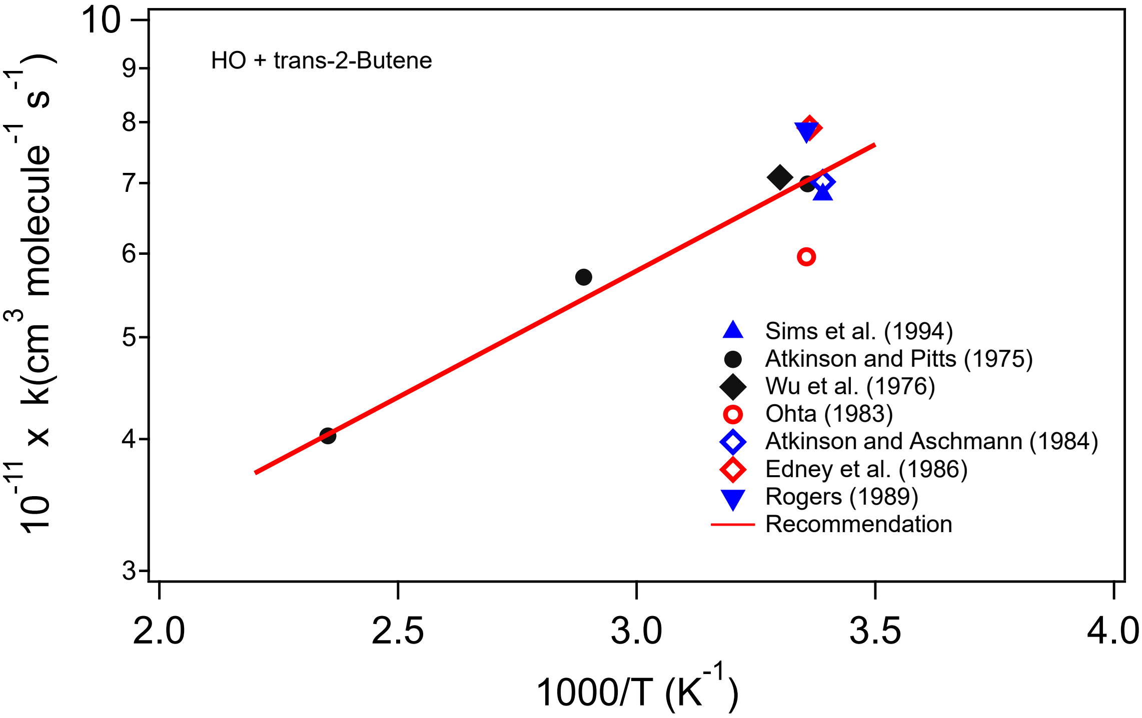

Rate coefficients for HO + *trans*-2-butene.

HOx_VOC66: biacetyl

Last evaluated: June 2009; Last change in preferred values: June 2009

$HO + CH_3C(O)C(O)CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	*Temp.*/K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.4\ ^{+0.8}\ _{-0.6}) \times 10^{-13}$	298	Darnall et al., 1979	FP-RF (a)
$(1.12\pm0.65) \times 10^{-12}$ exp[-(450±90)/T]	240-440	Dagaut et al., 1988	FP-RF (b)
$(2.3 \pm 0.2) \times 10^{-13}$	298		

Comments

(a) HO radicals were generated by the vacuum ultraviolet (λ ≥ 105 nm) photolysis of H_2O and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(b) HO radicals were generated by the vacuum ultraviolet (λ ≥ 165 nm) photolysis of H_2O and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	2.3×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	5.25×10^{-13} exp(-243/T)	240-350
Reliability		
Δ log k	± 0.06	298
Δ E/R	± 50	240-350

Comments on Preferred Values

The 298 K rate coefficient from the study of Darnall et al. (1979) is in excellent agreement with that of Dagaut et al. (1988). The combined data set of Darnall et al. at 298 K and those of Dagaut et al. below 350 K are used to derive the preferred values for the temperature dependence for atmospheric purposes.

The reaction of HO with 2,3-butanedione is assumed to proceed via H-atom abstraction from one of the methyl groups:

$$HO + CH_3C(O)C(O)CH_3 \rightarrow \quad H_2O + CH_3C(O)C(O)CH_2$$

leading to a peroxy radical after reaction with O_2 which can at least partly react with NO to form an alkoxy radical, that can either dissociate or react with O_2:

$$CH_3C(O)C(O)CH_2O \rightarrow CH_3C(O)C(O) + HCHO$$

$$CH_3C(O)C(O)CH_2O + O_2 \rightarrow CH_3C(O)C(O)CHO + HO_2$$

Christensen et al. (1998) have reported that the atmospheric fate of $CH_3C(O)C(O)CH_2O$ formed from the Cl-initiated oxidation of 2,3-butanedione is decomposition to give HCHO, CO, and $CH_3C(O)$ radicals. Hence, it is expected that the products of the reaction of HO with 2,3-butanedione under atmospheric conditions are $CH_3C(O)O_2$, HCHO and CO.

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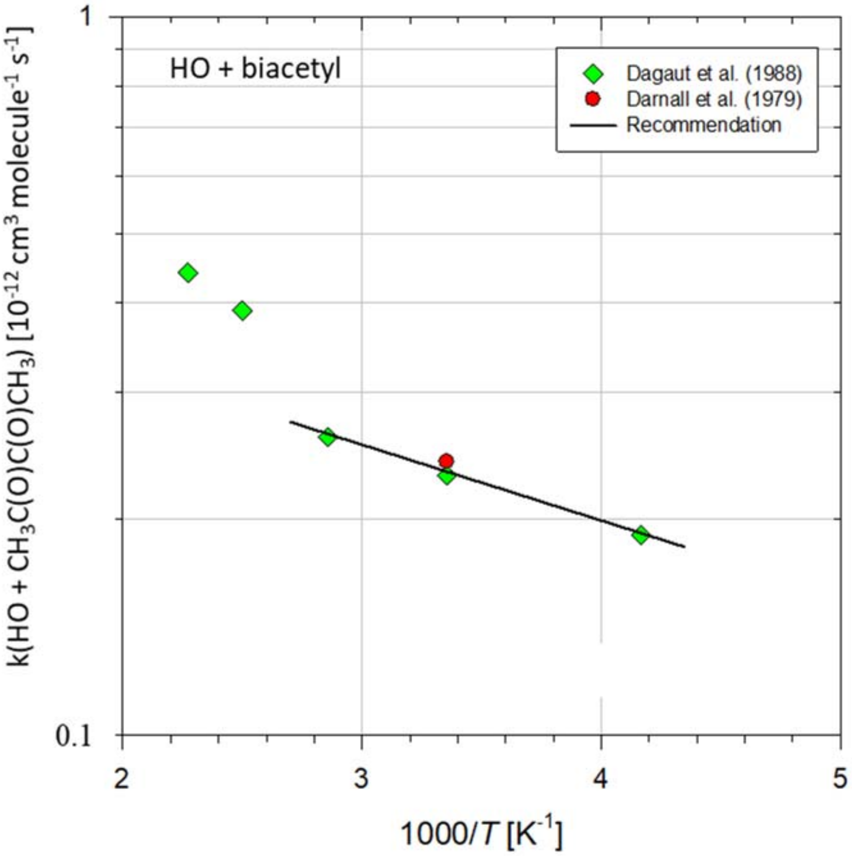

Rate coefficients for HO + biacetyl.

HOx_VOC67: *n*-butanoic acid

Last evaluated: March 2009; Last change in preferred values: March 2009

HO + *n*-$C_3H_7C(O)OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.8 \pm 0.16) \times 10^{-12}$	298	Zetzsch and Stuhl, 1982	FP-RF (a)

Comments

(a) HO radicals were generated by the vacuum ultraviolet ($\lambda \geq 105$ nm) photolysis of H_2O and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	1.8×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred rate coefficient value at 298 K is based on the sole study of Zetzsch and Stuhl (1982). This value is higher than those for the shorter chain organic acids ($CH_3C(O)OH$ and $C_2H_5C(O)OH$, respectively, $k = 7.4 \times 10^{-13}$ and 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

As with the other acids, it is expected that the reaction will occur both at the acidic site (–C(O)OH) and the alkyl site (*n*-C_3H_7-).

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HOx_VOC68: *i*-butanal

Last evaluated: June 2009; Last change in preferred values: June 2009

HO + *i*-$C_3H_7CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	*Temp.*/K	Reference	Technique/Comments
Absolute Rate Coefficients			
(6.8±0.3) × 10^{-12} exp[(393 ± 125)/*T*]	255-423	Semmes et al., 1985	FP-RF (a)
(2.42 ± 0.33) × 10^{-11}	298		
(15.8±0.5.0) × 10^{-12} exp[(313 ± 145)/*T*]	298-519	Dóbé et al., 1989	DF-RF (b)
(4.63 ± 0.73) × 10^{-11}	298		
(7.3±1.9) × 10^{-11} exp[(390 ± 78)/*T*]	243-372	Thévenet et al., 2000	PLP-LIF (c)
(2.6 ± 0.4) × 10^{-11}	298		
Relative Rate Coefficients			
(1.68 ± 0.20) × 10^{-11}	298	Audley et al., 1981	RR (d, h)
(2.69 ± 0.52) × 10^{-11}	298 ± 4	Kerr and Sheppard, 1981	RR (e, i)
(2.78 ± 0.26) × 10^{-11}	297 ± 3	Stemmler et al., 1997	RR (f, j)
(2.64 ± 0.22) × 10^{-11}	298 ± 2	D'Anna et al., 2001	RR (g, k)

Comments

(a) HO radicals were generated by the vacuum ultraviolet (λ ≥ 165 nm) photolysis of H_2O and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(b) HO radicals were generated by the reaction H + NO_2 and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(c) HO radicals were generated by the photolysis of H_2O_2 and their concentration was measured by pulsed laser induced fluorescence.

(d) HO radicals were generated by the dark reaction of H_2O_2-NO_2 mixtures in the presence of CO and an organic compound. From sequential experiments using acetaldehyde and *iso*-butyraldehyde, a rate coefficient ratio of *k*(HO + *iso*-butyraldehyde)/*k*(HO + acetaldehyde) = 1.12 ± 0.13 (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis using *k*(HO + acetaldehyde) = 1.5 × 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of HONO at λ = 300-450 nm in air at atmospheric pressure in a 220 L Tedlar chamber. The concentrations of *iso*-butyraldehyde and ethene (the reference compound) were measured by GC-FID. The measured rate coefficient ratio of *k*(HO + *iso*-butyraldehyde)/*k*(HO + ethene) = 3.40 ± 0.66 is placed on an absolute basis using *k*(HO + ethene) = 7.9 × 10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (IUPAC, 2019).

(f) HO radicals were generated by the photolysis of CH_3ONO at λ = 350-450 nm in air at 725 ± 25 Torr (967 ± 33 mbar) pressure in a 200 L Teflon chamber. The concentrations of *iso*-butyraldehyde and di-n-propyl ether (the reference compound) were measured by GC. The measured rate coefficient ratio of *k*(HO + *iso*-butyraldehyde)/*k*(HO + di-n-propyl ether) =

1.39 ± 0.04 is placed on an absolute basis using *k*(HO + di-n-propyl ether) = 2.0 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K and atmospheric pressure (Calvert et al., 2010).

(g) HO radicals were generated by the photolysis of an organic nitrite in air at 1013 ± 10 mbar (760 ± 7.5 Torr) pressure in a 250 L electropolished stainless-steel reactor. The concentrations of *iso*-butyraldehyde and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of *k*(HO + *iso*-butyraldehyde)/*k*(HO + 1-butene) = 0.85 ± 0.07 is placed on an absolute basis using *k*(HO + 1-butene) = 3.1 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K and atmospheric pressure of air (IUPAC, 2019).

(h) Relative to acetaldehyde

(i) Relative to ethene

(j) Relative to di-n-propyl ether

(k) Relative to isoprene

Preferred Values

Parameter	Value	*T*/K
k/ cm^3 $molecule^{-1}$ s^{-1}	2.6 × 10^{-11}	298
k/ cm^3 $molecule^{-1}$ s^{-1}	6.8 × 10^{-12} exp(410/*T*)	240-425
Reliability		
Δ log *k*	± 0.04	298
Δ E/R	± 60	240-425

Comments on Preferred Values

The measurements of Kerr and Sheppard (1981), Semmes et al. (1985), Stemmler et al. (1997), Thévenet et al. (2000) and D'Anna et al. (2001) at 298 K are in very good agreement. The values reported by Audley et al. (1981) and Dóbé et al. (1989) are, respectively, ~ 40% lower and ~ 70% larger than the others. The preferred 298 K rate coefficient is derived from the mean of the room temperature rate coefficients of Kerr and Sheppard (1981), Semmes et al. (1985), Stemmler et al. (1997), Thévenet et al. (2000) and D'Anna et al. (2001). The temperature dependence is obtained from a fit to the data other than those Audley et al. (1981) and Dóbé et al. (1989). The relative rate coefficient of Audley et al. (1981) was not used in the evaluation, due to questions concerning the applicability of the experimental technique used (Semmes et al., 1985).

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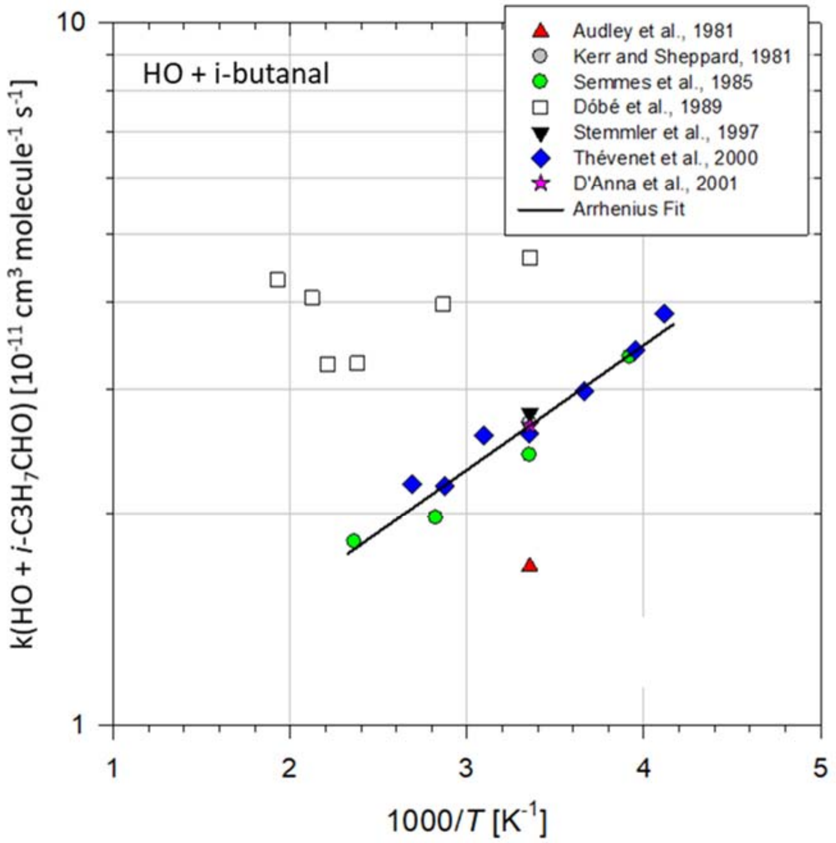

Rate coefficients for HO + *i*-butanal.

HOx_VOC69: 2-methyl-1-propanol

Last evaluated: June 2009; Last change in preferred values: June 2009

HO + $(CH_3)_2CHCH_2OH$ → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	*Temp.*/K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.1 \pm 0.9) \times 10^{-12} \exp[(352 \pm 82)/T]$	241-370	Mellouki et al., 2004	PLP-LIF (a)
$(9.2 \pm 0.4) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(8.8 \pm 0.3) \times 10^{-12}$	295 ± 2	Wu et al., 2003	RR (b, d)
$(9.2 \pm 0.4) \times 10^{-12}$	295 ± 2	Wu et al., 2003	RR (b, e)
$(8.5 \pm 0.1) \times 10^{-12}$	298 ± 2	Mellouki et al., 2004	RR (c, f)
$(8.8 \pm 0.3) \times 10^{-12}$	298 ± 2	Mellouki et al., 2004	RR (c, g)

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 and their concentration measured by pulsed laser induced fluorescence.

(b) HO radicals were generated by the photolysis of H_2O_2 in 1 atmosphere of air at 254 nm. Experiments were carried out in a ~100 liter Teflon chamber, and the concentrations of 2-methyl-1-propanol (isobutyl alcohol), propane and cyclohexane (the reference organics) were measured by GC-FID. The measured rate coefficient ratios of k(HO + $(CH_3)_2CHCH_2OH$)/k(HO + propane) and k(HO + $(CH_3)_2CHCH_2OH$)/k(HO + cyclohexane) are placed on an absolute basis using k(HO + propane) = 1.05×10^{-12} (Atkinson et al., 2006) and k(HO + cyclohexane) = 6.9×10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K (Calvert et al., 2008).

(c) HO radicals were generated by the photolysis of H_2O_2 in 1 atmosphere of air at 254 nm. Experiments were carried out in a ~120 liter Teflon chamber, and the concentrations of 2-methyl-1-propanol (isobutyl alcohol), 1-butanol and 1,3-dioxolane (the reference organics) were measured by GC-FID. The measured rate coefficient ratios of k(HO + $(CH_3)_2CHCH_2OH$)/k(HO + 1-butanol) = 1.00 ± 0.01 and k(HO + $(CH_3)_2CHCH_2OH$)/k(HO + 1,3-dioxolane) = 0.88 ± 0.03 are placed on an absolute basis using k(HO + 1-butanol) = 8.5×10^{-12} at 298 K (IUPAC, 2019), and k(HO + 1,3-dioxolane) = 1.0×10^{-11} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2008).

(d) Relative to HO + propane

(e) Relative to HO + cyclohexane

(f) Relative to HO + 1-butanol

(g) Relative to HO + 1,3-dioxolane

Preferred Values

Parameter	Value	*T*/K
k/cm^3 molecule^{-1} s^{-1}	8.9×10^{-12}	298
k/cm^3 molecule^{-1} s^{-1}	$2.73 \times 10^{-12} \exp(352/T)$	240-370
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 120	240-370

Comments on Preferred Values

The 298 K rate coefficients values from the absolute and relative studies of Mellouki et al. (2004) are in very good agreement with those from the relative determination of Wu et al. (2003). The preferred rate coefficient value at 298 K is derived from the average of the measurements reported in these two studies. The absolute rate study of Mellouki et al. (2004), the sole temperature-dependence study, combined with the preferred 298 K is used to derive E/R.

The reaction of HO with 2-methyl-1-propanol is expected to proceed via H-atom abstraction from $–CH_2–$ and $>CH–$ groups with a lower contribution from the CH_3–groups.

$HO + (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2CHCH_2O$ (a)
$HO + (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2CHCHOH$ (b)
$HO + (CH_3)_2CHCH_2OH \rightarrow H_2O + (CH_3)_2CCH_2OH$ (c)
$HO + (CH_3)_2CHCH_2OH \rightarrow H_2O + CH_2CH(CH_3)CH_2OH$ (d)

The α-hydroxy alkyl radical formed by H-atom abstraction from $–CH_2–$ group (channel b) reacts with O_2 to form 2-methyl propanal ($(CH_3)_2CHCHO$). The hydroxyl alkyl radicals formed in channels (c) and (d) will add O_2 then react with NO to give the alkoxy radicals $(CH_3)_2C(O)CH_2OH$ and $OCH_2CH(CH_3)CH_2OH$. $(CH_3)_2C(O)CH_2OH$ radicals decompose to give acetone and formaldehyde. $OCH_2CH(CH_3)CH_2OH$ radicals react with O_2 to give $HC(O)CH(CH_3)CH_2OH$ and decompose to give $2HCHO + CH_3CHO$.

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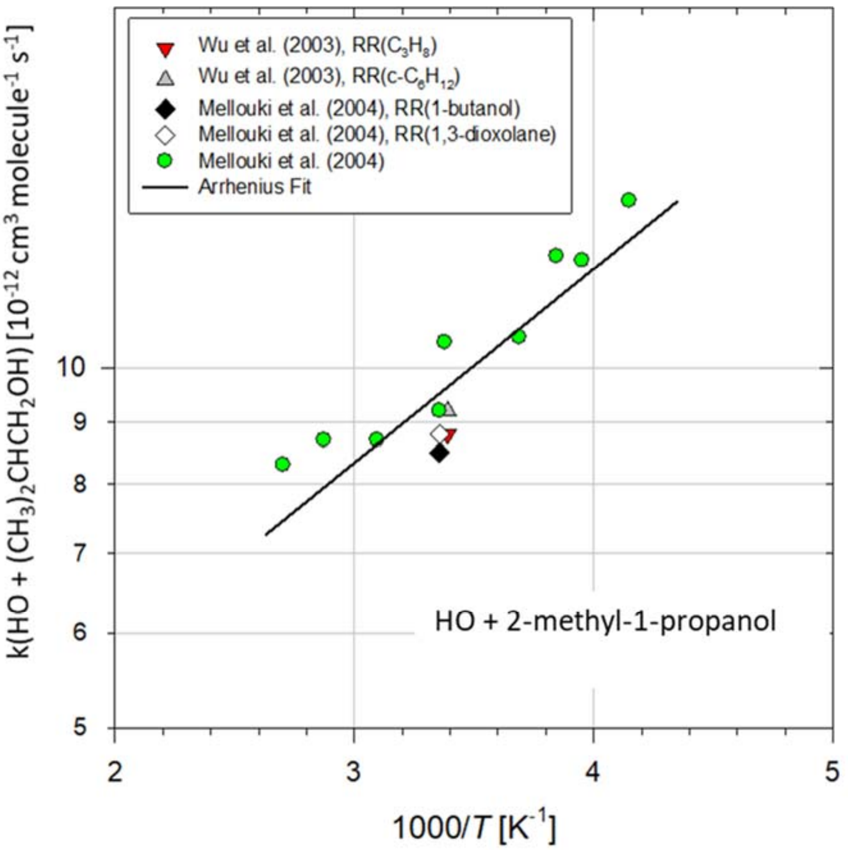

Rate coefficients for HO + 2-methyl-1-propanol.

HOx_VOC70: 2-methyl-2-propanol

Last evaluated: June 2009; Last change in preferred values: June 2009

HO + $(CH_3)_3COH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	*Temp.*/K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.3 \pm 1.6) \times 10^{-12} \exp[-(310 \pm 150)/T]$	240-440	Wallington et al., 1988	FP-RF (a)
$(1.07 \pm 0.08) \times 10^{-12}$	298		
$(8.1 \pm 1.7) \times 10^{-13}$	298	Saunders et al., 1994	DF-LIF (b)
$(2.66 \pm 0.48) \times 10^{-12} \exp[-(270 \pm 130)/T]$	253-372	Téton et al., 1996	PLP-LIF (c)
$(1.08 \pm 0.10) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(1.08 \pm 0.07) \times 10^{-12}$	295 ± 2	Wu et al., 2003	RR (d)

Comments

(a) HO radicals were generated by the vacuum ultraviolet ($\lambda \geq 165$ nm) photolysis of H_2O and monitored as function of time under pseudo-first order conditions by resonance fluorescence.

(b) HO radicals were generated by the H + NO_2 reaction and monitored under pseudo-first order conditions by laser induced fluorescence.

(c) HO radicals were generated by the photolysis of H_2O_2 and their concentration measured by pulsed laser induced fluorescence.

(d) HO radicals were generated by the photolysis of H_2O_2 in 1 atmosphere of air at 254 nm. Experiments were carried out in a ~100 liter Teflon chamber, and the concentrations of t-butyl alcohol and propane (the reference organic) were measured by GC-FID. The measured rate coefficient ratio of $k(HO + (CH_3)_3COH)/k(HO + \text{propane})$ is placed on an absolute basis using $k(HO + \text{propane}) = 1.05 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 K (IUPAC, 2019).

Preferred Values

Parameter	**Value**	***T*/K**
k/ molecule^{-1} s^{-1}	1.1×10^{-12}	298
k/ cm^3 molecule^{-1} s^{-1}	$1.6 \times 10^{-12} \exp(-121/T)$	240-314
Reliability		
$\Delta \log k$	± 0.06	298
$\Delta E/R$	± 75	240-314

Comments on Preferred Values

The rate coefficient values obtained by Wallington et al. (1988), Téton et al. (1996) and Wu et al. (2003) near 298 K are in very good agreement. The room temperature value of

Saunders et al. (1994) is ~25% lower than the others. The Arrhenius plots of the data of Wallington et al. (1988) and Téton et al. (1996) show curvature, fitting the expression k = B + C exp(-D/T) to the rate coefficients reported by these authors gives $k = 9.57\times10^{-13} + 5.65\times10^{-11} \exp(-1836/T)$ cm^3 $molecule^{-1}$ s^{-1} over the temperature range 240-440 K. For atmospheric purposes, a fit to the data below 314 K of Wallington et al., Téton et al., and Wu et al. yields $k = 1.6 \times 10^{-12} \exp(-121/T)$, giving $k = 1.1 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

The reaction of HO radicals with 2-methyl-2-propanol proceeds mainly by H-atom from CH_3- group. Under atmospheric conditions and in the presence of NO, the main degradation products expected are formaldehyde and acetone (Japar et al., 1990):

$$(CH_3)_3COH + HO + NO (+O_2) \rightarrow H_2CO + CH_3C(O)CH_3 + HO_2 + NO_2$$

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IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
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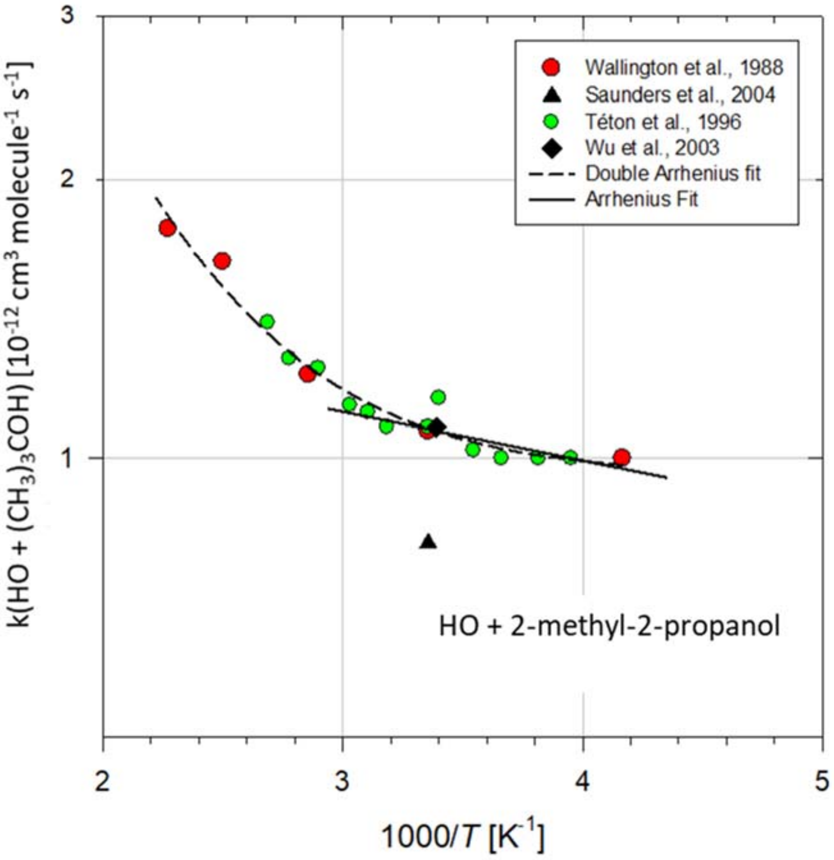


Rate coefficients for HO + 2-methyl-2-propanol.

HOx_VOC76: 2-hydroxybutanal

Last evaluated: June 2016; Last change in preferred values: June 2016

$$\mathbf{HO + C_2H_5CH(OH)CHO \rightarrow H_2O + C_2H_5CH(OH)CO} \qquad (1)$$
$$\mathbf{HO + C_2H_5CH(OH)CHO \rightarrow H_2O + C_2H_5C(OH)CHO} \qquad (2)$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	*Temp.*/K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.37 \pm 0.23) \times 10^{-11}$	296 ± 2	Baker et al., 2004	RR-GC (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at 986 mbar (740 Torr) total pressure of purified air at > 300 nm. Experiments were carried out in a 7500 liter Teflon chamber. 2-hydroxybutanal was generated in situ from the HO radical-initiated reaction of 1,2-butanediol. The concentrations of 2-hydroxybutanal and its precursor, 1,2-butanediol, were measured by gas chromatography. From comparison of the measured time-concentration behaviour of $C_2H_5CH(OH)CHO$ and its precursor a rate coefficient ratio of k(HO + 2-hydroxybutanal)/k(HO + 1,2-butanediol) = 0.944 ± 0.074 was derived. This rate coefficient ratio is placed on an absolute basis using k(HO + 1,2-butanediol) = 2.51×10^{-11} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2011).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	2.4×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Value

The recommendation is based upon the relative study by Baker et al. (2004). The possible channels for reaction of $C_2H_5CH(OH)CHO$ with HO are:

$$\begin{aligned} HO + CH_3CH_2CH(OH)CHO &\rightarrow CH_3CH_2CH(OH)CO + H_2O && (1)\\ &\rightarrow CH_3CH_2C(OH)CHO + H_2O && (2)\\ &\rightarrow CH_3CHCH(OH)CHO + H_2O && (3)\\ &\rightarrow CH_2CH_2CH(OH)CHO + H_2O && (4)\\ &\rightarrow CH_3CH_2CH(O)CHO + H_2O && (5) \end{aligned}$$

The channels (3), (4) and (5) are expected to be of minor importance compared to the channels (1) and (2). Hence, the reaction is expected to proceed mainly via abstraction of the aldehydic hydrogen to give $C_2H_5CH(OH)CO$ radicals (channel (1)) and through the H-atom abstraction from the >CH- group in the α-position to the hydroxyl group leading to $C_2H_5C(OH)CHO$ radicals (channel (2)) similarly to the reaction of HO with hydroxyacetaldehyde ($HOCH_2CHO$).

References

Baker, J., Arey, J. and Atkinson, R.: J. Phys. Chem. A, 108, 7032, 2004.

Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J. and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2011.

HOx_VOC77: 1-nitrooxy-2-butanol

Last evaluated: June 2016; Last change in preferred values: June 2016

$HO + C_2H_5CH(OH)CH_2ONO_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	*Temp.*/K	Reference	Technique/Comments
Relative Rate Coefficients			
$(7.0 \pm 1.4) \times 10^{-12}$	296 ± 2	Treves and Rudich, 2003	RR (a, b)

Comments

(a) The rate coefficient was measured at atmospheric pressure of dry synthetic air in a photochemical reactor (100 L Tedlar chamber) by the relative rate technique using solid-phase microextraction (SPME) coupled to gas chromatography (GC) for the detection of the organic reactants. HO radicals were generated by the photolysis of CH_3ONO (or C_2H_5ONO)-NO-air + 1-nitrooxy-2-butanol + 1-pentanol (or 1-octanol) mixtures at wavelengths > 300 nm. The measured rate coefficient ratios of k(HO + 1-nitrooxy-2-butanol)/k(HO + 1-pentanol) and k(HO + 1-nitrooxy-2-butanol)/k(HO + 1-octanol) were not given by the authors, they were placed on an absolute basis using k(HO + 1-pentanol) = $(1.12 \pm 0.15) \times 10^{-11}$ and k(HO + 1-octanol) = $(1.44 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Nelson et al., 1990).

(b) Average of the data obtained relative to HO + 1-pentanol and HO + 1-octanol.

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	7.0×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.20	298

Comments on Preferred Values

The preferred value is an average of the relative rate coefficients of Treves and Rudich (2003) obtained with two reference compounds. The reaction of HO with $C_2H_5CH(OH)CH_2ONO_2$ is expected to proceed mainly via H-atom abstraction from the CH group in the α-position to the hydroxyl group leading to $C_2H_5C(OH)CH_2ONO_2$ radicals which reacts with O_2 leading to HO_2 and the corresponding carbonyl ($C_2H_5C(O)CH_2ONO_2$).

$$HO + C_2H_5CH(OH)CH_2ONO_2 \rightarrow C_2H_5C(OH)CH_2ONO_2 + H_2O \quad (1)$$

$$O_2 + C_2H_5C(OH)CH_2ONO_2 \rightarrow C_2H_5C(O)CH_2ONO_2 + HO_2 \quad (2)$$

References

Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J. and Nielsen, O.J.: Int. J. Chem. Kinet., 22, 1111, 1990.
Treves, K. and Rudich, Y.: J. Phys. Chem. A, 107, 7809, 2003.

HOx_VOC78: 2-nitrooxy-2-butanol

Last evaluated: June 2016; Last change in preferred values: June 2016

$HO + C_2H_5CH(ONO_2)CH_2OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	*Temp.*/K	Reference	Technique/Comments
Relative Rate Coefficients			
$(7.4 \pm 1.5) \times 10^{-12}$	296 ± 2	Treves and Rudich, 2003	RR (a)

Comments

(a) The rate coefficient was measured at atmospheric pressure of dry synthetic air in a photochemical reactor (100 L Tedlar chamber) by the relative rate technique using solid-phase microextraction (SPME) coupled to gas chromatography (GC) for the detection of the organic reactants. HO radicals were generated by the photolysis of CH_3ONO (or C_2H_5ONO)-NO-air + 2-nitrooxy-1-butanol + 1-pentanol (or 1-octanol) mixtures at wavelengths > 300 nm. The measured rate coefficient ratios of k(HO + 2-nitrooxy-1-butanol)/k(HO + 1-pentanol) and k(HO + 2-nitrooxy-1-butanol)/k(HO + 1-octanol) were not given by the authors, they were placed on an absolute basis using k(HO + 1-pentanol) = $(1.12 \pm 0.15) \times 10^{-11}$ and k(HO + 1-octanol) = $(1.44 \pm 0.15) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Nelson et al., 1990). The value in the table is the average of the data obtained relative to HO + 1-pentanol and HO + 1-octanol.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	7.4×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.20	298

Comments on Preferred Values

The preferred value is an average of the relative rate coefficients of Treves and Rudich (2003) obtained with two reference compounds. The reaction of HO with $C_2H_5CH(ONO_2)CH_2OH$ is expected to proceed mainly via H-atom abstraction from the CH_2 group in the α-position to the hydroxyl group leading to $C_2H_5C(ONO_2)CH_2OH$ radicals which react with O_2 leading to HO_2 and the corresponding carbonyl ($C_2H_5C(ONO_2)CHO$).

$$HO + C_2H_5CH(ONO_2)CH_2OH \rightarrow C_2H_5CH(ONO_2)CHOH + H_2O \quad (1)$$

$$O_2 + C_2H_5CH(ONO_2)CHOH \rightarrow C_2H_5CH(ONO_2)CHO + HO_2 \quad (2)$$

References

Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J. and Nielsen, O.J.: Int. J. Chem. Kinet., 22, 1111, 1990.
Treves, K. and Rudich, Y.: J. Phys. Chem. A, 107, 7809, 2003.

HOx_VOC79: 3-hydroxy-2-butanone

Last evaluated: June 2016; Last change in preferred values: June 2016

$$\mathbf{HO + CH_3C(O)CH(OH)CH_3 \rightarrow H_2O + CH_3C(O)C(OH)CH_3} \quad \mathbf{(1)}$$
$$\mathbf{HO + CH_3C(O)CH(OH)CH_3 \rightarrow products} \quad \mathbf{(2)}$$

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/Comments
Relative Rate Coefficients			
$(9.3 \pm 2.0) \times 10^{-12}$	296 ± 2	Aschmann et al., 2000	RR-GC (a)
$(2.25 \pm 0.20) \times 10^{-12} \exp[(612 \pm 50)/T]$	298-338	Messaadia et al., 2013	RR-FTIR (b)
$(10.1 \pm 3.2) \times 10^{-12}$	298		

Comments

(a) HO radicals were generated by the irradiation of CH_3ONO-NO-air mixtures at 986 mbar (740 Torr) total pressure of purified air at ~5% humidity at $\lambda > 300$ nm. Experiments were carried out in a 7900 liter Teflon chamber. The concentrations of 3-hydroxy-2-butanone and n-octane (the reference compound) were measured by gas chromatography. The measured rate coefficient ratio of k(HO + 3-hydroxy-2-butanone)/k(HO + n-octane) = 1.19 ± 0.05 is placed on an absolute basis using k(HO + n-octane) = 7.81×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K and atmospheric pressure (Calvert et al., 2008).

(b) HO radicals were generated by the irradiation of HONO-air mixtures at 800-1013 mbar (600-760 Torr) of air at $400 > \lambda > 300$ nm. Experiments were carried out in a 63 liter triple-jacket Pyrex chamber. The concentrations of 3-hydroxy-2-butanone and benzaldehyde (the reference compound) were measured by FTIR. The measured rate coefficient ratio of k(HO + 3-hydroxy-2-butanone)/k(HO + benzaldehyde) = 0.80 ± 0.05 (at 298K), 0.70 ± 0.03 (at 313K), 0.72 ± 0.06 (at 338K) are placed on an absolute basis using k(HO + benzaldehyde) = $6.8 \times 10^{-12} \exp(185/T)$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2011).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	9.7×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	$1.24 \times 10^{-12} \exp(612/T)$	280-350
Reliability		
$\Delta \log k$	± 0.10	298
$\Delta E/R$	± 350	280-350

Comments on Preferred Values

The results reported by Aschmann et al. (2000) and Messaadia et al. (2013) are in good agreement. Taking an average of the results from the two studies gives the recommended value of $k = 9.7 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K. Fitting the Arrhenius expression to the data from

Messaadia et al. (2013) and adjusting the A-factor to reproduce the recommended value at 298 K gives $k(HO+CH_3C(O)CH(OH)CH_3) = 1.24 \times 10^{-12} \exp(612/T)$ cm^3 molecule^{-1} s^{-1}. In the product study by Aschmann et al. (2000) of the HO initiated oxidation of 3-hydroxy-2-butanone it was observed that 2,3-butanedione (biacetyl) was formed in a molar yield of 0.79 ± 0.14. The reaction proceeds mainly via hydrogen atom abstraction from the tertiary C-H bond:

$$HO + CH_3C(O)CH(OH)CH_3 \rightarrow CH_3C(O)C(OH)CH_3 + H_2O$$
$$CH_3C(O)C(OH)CH_3 + O_2 \rightarrow CH_3C(O)C(O)CH_3 + HO_2$$

The other possible channel is the H-atom abstraction from the methyl group which may account for about 20 %.

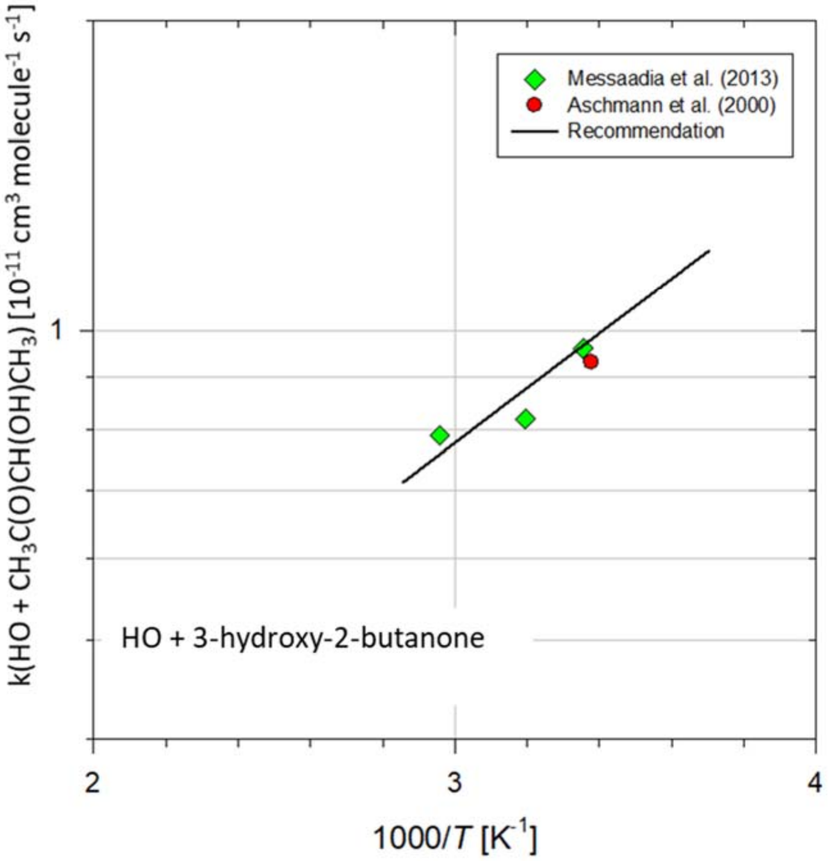
References

Aschmann, S. M., Arey, J. and Atkinson, R.: J. Phys. Chem. A, 104, 3998, 2000.

Calvert, J. G., Derwent, R. G., Orlando, J. J., Tyndall, G. S. and Wallington, T. J.: *The Mechanisms of Atmospheric Oxidation of the Alkanes*, Oxford University Press, New York, 2008.

Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J. and Wallington, T. J.: *The Mechanisms of Atmospheric Oxidation of the Oxygenates*, Oxford University Press, New York, 2011.

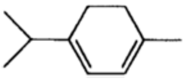
Messaadia, L., El Dib, G., Cazaunau, M., Roth, E., Ferhati, A., Mellouki, A. and Chakir, A.: Atmos. Env., 77, 951, 2013.



Rate coefficients for HO + 3-hydroxy-2-butanone.

HOx_VOC84: α-terpinene

Last evaluated: June 2014; Last change in preferred values: June 2014

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(3.53 \pm 0.39) \times 10^{-10}$	294±1	Atkinson et al., 1986	RR (a)
$(3.4 \pm 0.4) \times 10^{-10}$	290	Peeters et al., 1999	FT-MS (b)

α-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,3-diene.

Comments

(a) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. HO radical was generated by the photolysis of CH_3ONO at wavelengths > 300 nm. Correction made to the α-terpinene loss rate due to reaction with NO_2 was 24 to 65 % (generally ≈30%). α-terpinene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, k(HO + α-terpinene) / k(HO + 2,3-dimethyl-2-butene) = 3.21 ± 0.35 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(b) Flow tube at ≈2.7 mbar (2 Torr) of He. HO was generated by the reaction H+NO_2. α-terpinene and isoprene (reference reactant) were monitored by mass spectrometry in excess of HO radicals. The rate constant ratio obtained, k(HO + α-terpinene) / k(HO + isoprene) is not provided by the authors. The rate coefficient value was placed on an absolute basis using k(HO + isoprene) = 1.0×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

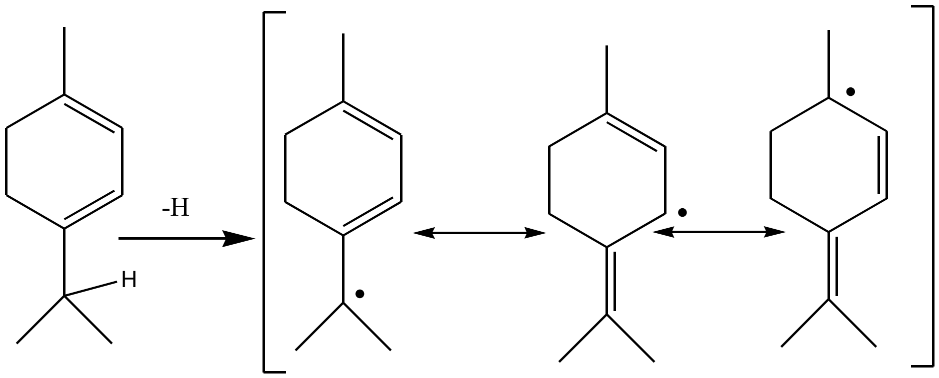
Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.5×10^{-10}	298
Reliability		
$\Delta \log k$	0.08	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate studies of Atkinson et al. (1986) and Peeters et al. (1999).

The reaction proceeds by addition of the HO radical to the >C=C< double bonds and by H-atom abstraction from the various C-H bonds with the HO radical addition channel expected to be the dominant channel. Reissell et al. (1999) have observed acetone (≈ 10%) as a reaction product but could not determine the reaction pathways leading to its formation. Both, HO-addition and H-abstraction could be involved. Peeters et al. (1999) reported a yield of (30±8)% for H-atom abstraction from all of the non-vinylic C-H bonds in the α-terpinene molecule. Hydrogen abstraction is facilitated by stabilization of the resulting radical by "super allyl" resonance delocalizing the unpaired electron over three C-atoms as shown in the scheme below (Vereecken and Peeters, 2001). Aschmann et al. (2011) suggested that H-abstraction from α-terpinene and γ-terpinene occur at similar rates. In their study of the HO reaction with γ-terpinene, they have shown that this reaction leads to p-cymene formation at least partly from H-atom abstraction from the two CH_2 groups in the 6-member ring. Lee et al. (2006) reported the following molar product yields from the HO-initiated oxidation of α-terpinene in the presence of NO_x: α-terpinaldehyde (19±2%), HCHO (7.8±2%), CH_3CHO (0.7±0.1%), HCOOH (6.1±1%), $CH_3C(O)CH_3$ (3.1±4%) and $CH_3C(O)OH$ (2±0.3%).



References

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Atkinson, R., Aschmann, S. M. and Pitts, J. N.: Int. J. Chem. Kinet., 18, 287-299, 1986.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C. and Seinfeld, J. H.: J. Geophys. Res., 111, D17305, 2006.
Peeters, J., Vandenberk, S., Piessens, E. and Pultau, V.: Chemosphere, 38, 1189-1195, 1999.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869-13879, 1999.

HOx_VOC85: γ-terpinene

Last evaluated: June 2014; Last change in preferred values: June 2014

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.73 \pm 0.18) \times 10^{-10}$	294±1	Atkinson et al., 1986	RR (a)

γ-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,4-diene.

Comments

(a) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. HO radical was generated by the photolysis of CH_3ONO at wavelengths > 300 nm. γ-terpinene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, k(HO + γ-terpinene) / k(HO + 2,3-dimethyl-2-butene) = 1.57 ± 0.16 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.7×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1986).

The reaction proceeds by addition of the HO radical to the >C=C< double bonds and by H-atom abstraction from the various C-H bonds with the addition channel being expected to be dominant. Rio et al. (2010) reported a branching ratio of (31±9%) for the H-atom abstraction channel. Reissell et al. (1999) observed acetone as a reaction product (10±3% molar yield) but could not ascribe the reaction pathways leading to its formation; HO-addition and H-abstraction could both be involved. Aschmann et al. (2011) observed p-cymene [1-methyl-4-(1-methylethyl)benzene or 4-isopropyltoluene] as a product from the reaction of HO with γ-terpinene with a molar yield of 13.6±2.5%. They suggested that p-cymene is formed after H-abstraction from the two ring CH_2 groups. Lee et al. (2006) observed γ-terpinaldehyde (57±6%), HCHO

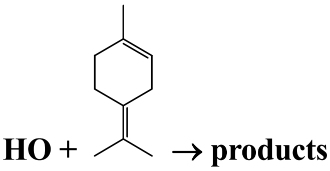
(17±2%), CH_3CHO (1.2±0.2%), HCOOH (8.3±0.8%), $CH_3C(O)CH_3$ (5.3±0.5%) and $CH_3C(O)OH$ (4.5±0.5%) as products of HO- radical initiated oxidation of γ-terpinene in the presence of NO_x.

References

Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 45, 4408-4411, 2011.
Atkinson, R., Aschmann, S. M. and Pitts, J. N.: Int. J. Chem. Kinet., 18, 287-299, 1986.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C. and Seinfeld, J. H.: J. Geophys. Res., 111, D17305, 2006.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869-13879, 1999.
Rio, C., Flaud, P-M., Loison, J-C. and Villenave, E.: Chem. Phys. Chem., 11, 3962-3970, 2010.

HOx_VOC86: terpinolene

Last evaluated: June 2014; Last change in preferred values: June 2014



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Technique/Comments
Relative Rate Coefficients			
$(2.21 \pm 0.56) \times 10^{-10}$	295 ± 2	Corchnoy and Atkinson, 1990	RR-GC (a)

Terpinolene is 4-isopropylidene-1-methyl-cyclohexene

Comments

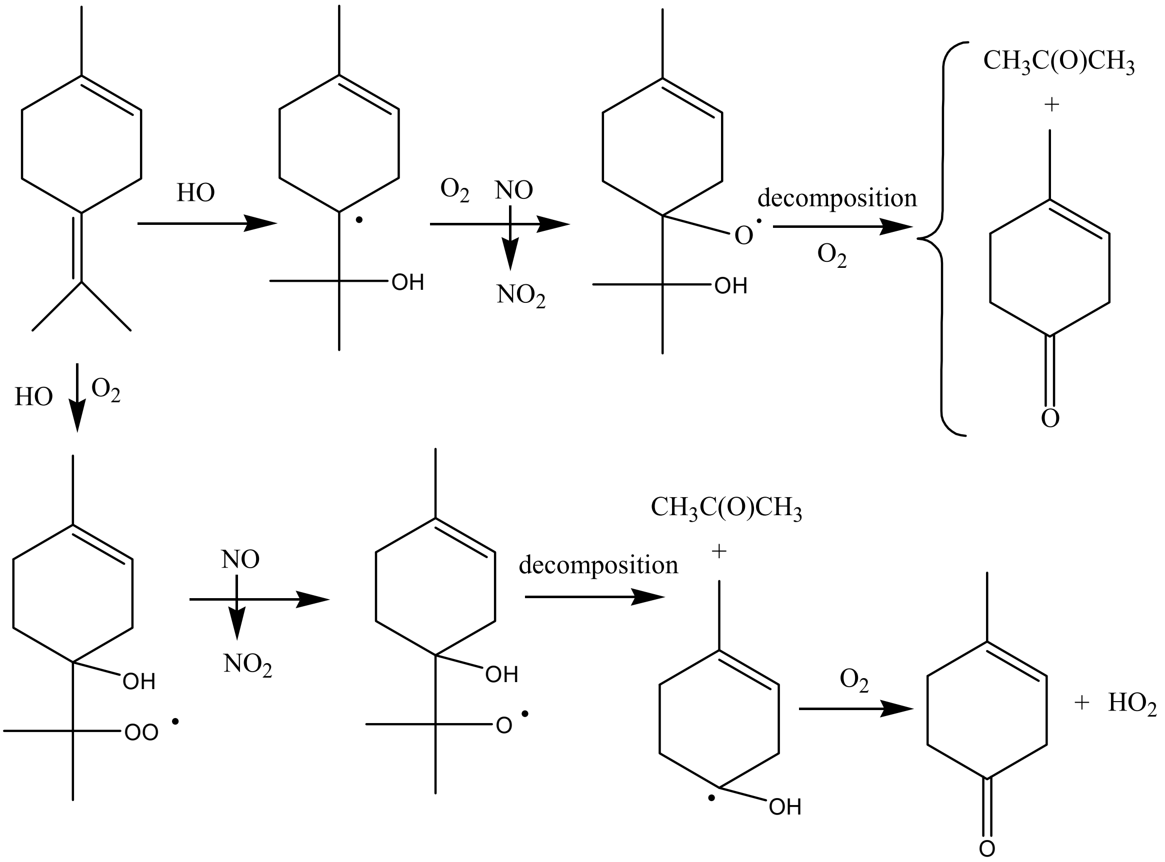
(a) 6400 L Teflon chamber at 735 Torr (980 mbar) of air. HO was generated using the photolysis of CH_3ONO at wavelengths of >300 nm. Terpinolene and isoprene (reference reactant) were monitored by GC-FID. The rate constant ratio k(HO + terpinolene) / (k(HO + isoprene) = 2.21 ± 0.09 is placed on an absolute basis using k(HO + isoprene) = 1.0×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.2×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the single relative rate study of Corchnoy and Atkinson (1990). The error limits are expanded to reflect the single measurement. The reaction proceeds almost entirely by HO radical addition to the C=C bonds in terpinolene. Hakola et al. (1994) identified 4-methyl-3-cyclohexen-1-one as a major product from the reaction of HO radical with terpinolene in presence of NOx with a yield of (26±6) %. Acetone has been reported to be formed with a yield of 32-39 % (Reissell et al., 1999, Orlando et al., 2000) which is similar to the measured yield of the co-product 4-methyl-3-cyclohexen-1-one (reaction scheme given below). Hakola et al. (1994) observed another product with a minor yield of (8±2) % which was tentatively identified as a keto-aldehyde compound ($(CH_3)_2C=C(CH_2CHO)CH_2CH_2C(O)CH_3$) arising from the addition of HO to the endocyclic C=C bond (Hakola et al., 1994). Orlando et al. (2000) identified formaldehyde and formic acid as reaction products with yields of (29±6%) and (8±2%), respectively. Lee at al. (2006) reported a yield of 31% for secondary organic aerosol (SOA) formation along with organic compounds such as HCHO (23±3%), CH_3CHO (0.7±0.1%), HCOOH (3.5±0.7%), $CH_3C(O)CH_3$ (20±2%) and $CH_3C(O)OH$ (1±0.2%).



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Corchnoy, S. B. and Atkinson, R., Env. Sci. Tech., 24, 1497-1502, 1990.
Hakola, H., Arey, J., Aschmann, S. and Atkinson, R., J. Atmos. Chem., 18, 75-102, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
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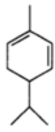
Orlando, J.J., Nozière, B., Tyndall, G.S., Orzechowska, G.E., Paulson, S.E. and Rudich, Y., J. Geophys. Res., 105, 11561-11572, 2000.
Reissell, A., Harry, C., Aschmann, S.M., Atkinson, R. and Arey, J., J. Geophys. Res., 104, 13869-13879, 1999.

HOx_VOC87: α-phellandrene

Last evaluated: June 2014; Last change in preferred values: June 2014

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(3.05 \pm 0.70) \times 10^{-10}$	294±1	Atkinson et al., 1986	RR (a)
$(3.3 \pm 0.4) \times 10^{-10}$	290	Peeters et al., 1999	FT-MS (b)

α-phellandrene is 2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene.

Comments

(a) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. HO radical was generated by the photolysis of CH_3ONO at wavelengths > 300 nm. α-phellandrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. Correction made to the α-phellandrene loss rate due to reaction with NO_2 was 15 to 59 % (generally ≈50%). The rate constant ratio, k(HO + α- phellandrene) / k(HO + 2,3-dimethyl-2-butene) = 2.77 ± 0.63 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(b) Flow tube at ≈2.7 mbar (2 Torr) of He. HO was generated by the reaction H+NO_2. α-phellandrene and isoprene (reference reactant) were monitored by mass spectrometry in excess of HO radicals. The rate constant ratio obtained, k(HO + α-phellandrene) / k(OH + isoprene) is not provided by the authors. The rate coefficient value was placed on an absolute basis using k(HO + isoprene) = 1.0×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

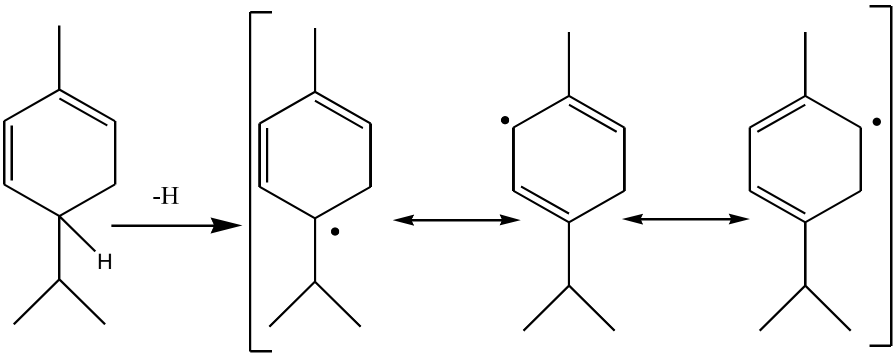
Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.2×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.08	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate studies of Atkinson et al. (1986) and Peeters et al. (1999).

The reaction proceeds by initial addition of the HO radical to the carbon atoms of the C=C bonds and by H-atom abstraction from the various C-H bonds with the OH radical addition channel being expected to be dominant. Reissell et al. (1999) have observed acetone (8±4%) as a reaction product but could not determine the reaction pathways leading to its formation. Both, HO-addition and H-abstraction could be involved. Peeters et al. (1999) have reported a yield of (27±10)% for H-atom abstraction through the direct observation of H_2O as reaction product. H-atom abstraction is expected to occur mainly from the non-vinylic C-H bonds and CH_2 group in the ring with H-atom abstraction from the methyl and isopropyl substituent groups being of minor importance since the tertiary C-H bond in the isopropyl group is not allylic. The hydrogen abstraction is facilitated by stabilization of the resulting radical by “super allyl” resonance delocalizing the unpaired electron over three C-atoms as shown in the scheme (Vereecken and Peeters, 2001, Aschmann et al., 2011).



References

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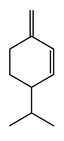
Atkinson, R., Aschmann, S. M. and Pitts, J. N.: Int. J. Chem. Kinet., 18, 287-299, 1986.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Peeters, J., Vandenberk, S., Piessens, E. and Pultau, V.: Chemosphere, 38, 1189-1195, 1999.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869-13879, 1999.
Vereecken, L. and Peeters, J.: Chem. Phys. Letters, 333, 162-168, 2001.

HOx_VOC88: β-phellandrene

Last evaluated: June 2014; Last change in preferred values: June 2014

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.66 \pm 0.41) \times 10^{-10}$	297±2	Shorees et al., 1991	RR (a)

β-phellandrene is 3-isopropyl-6-methylene-cyclohexene.

Comments

(a) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. HO radical was generated by the photolysis of CH_3ONO at wavelengths > 300 nm. β-phellandrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. Correction made to the β-phellandrene loss rate due to reaction with NO_2 was <32 % (typically 10-20%). β-phellandrene concentrations were corrected to account for the presence of a co-eluting limonene impurity, initially present at 9.8 % of the β-phellandrene concentration. The rate constant ratio, k(HO + β-phellandrene) / k(HO + 2,3-dimethyl-2-butene) = 1.51 ± 0.20 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

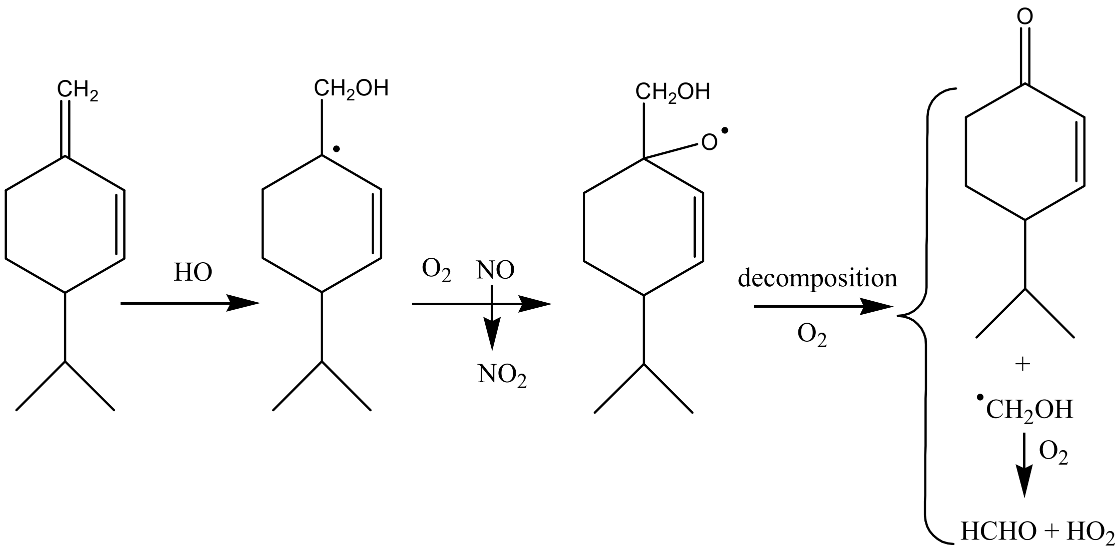
Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.7×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shorees et al. (1991) with increased uncertainties reflecting the difficulties of the experiment and the single measurement.

The reaction proceeds by initial addition of the HO radical to the carbon atoms of the C=C bonds and by H-atom abstraction from the various C-H bonds with the HO radical addition channel being expected to be the dominant. Hakola et al. (1999) have identified 4-isopropyl-2-cyclohexen-1-one as a product of the reaction with a formation yield of (29±7%). 4-Isopropyl-2-cyclohexen-1-one is expected to be produced through the initial HO addition at the acyclic >C=C< bond as shown below:

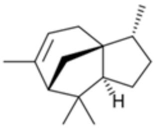


References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Hakola, H., Shorees, B., Arey, J. and Atkinson R.: Environ. Sci. Technol., 27, 278-283, 1993.
Shorees, B., Atkinson, R. and Arey, J.: Int. J. Chem. Kinet., 23, 897-906, 1991.

HOx_VOC89: α-cedrene

Last evaluated: June 2014; Last change in preferred values: June 2014

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(6.7 \pm 1.4) \times 10^{-11}$	296±2	Shu and Atkinson, 1995	RR (a)

α-Cedrene is (1S,2R,5S,7R)-2,6,6,8-tetramethyltricyclo[5.3.1.0^{1,5}]undec-8-ene

Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of CH_3ONO at wavelengths > 300 nm. α-Cedrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, k(HO + α-cedrene) / k(HO + 2,3-dimethyl-2-butene) = 0.608 ± 0.017 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	6.7×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Values

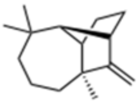
The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995). The reaction is expected to proceed predominantly by addition to the >C=C< double bond.

References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Shu, Y. and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

HOx_VOC90: longifolene

Last evaluated: June 2014; Last change in preferred values: June 2014

HO +  → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(4.7 \pm 1.0) \times 10^{-11}$	296±2	Shu and Atkinson, 1995	RR (a)

Longifolene is (1R,2S,7S,9S)- 3,3,7-trimethyl- 8-methylenetricyclo- [5.4.0.0^{2,9}]undecane

Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of CH_3ONO at wavelengths > 300 nm. Longifolene and *trans*-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, k(HO + longifolene) / k(HO + *trans*-2-butene) = 0.729 ± 0.025 is placed on an absolute basis using k(HO + *trans*-2-butene) = 6.4×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	4.7×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995). The reaction is expected to proceed predominantly by addition to the >C=C< double bond. The HO-initiated oxidation mechanism of longifolene is complex with many different pathways that produce a large number of organic compounds. Lee et al. (2006) reported molar product yields for HCHO (25±3%), CH_3CHO (3.7±0.4%), HCOOH (31±3%), $CH_3C(O)CH_3$ (3.8±0.3%) and $CH_3C(O)OH$ (15±1%).

References

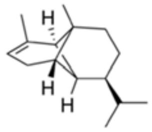
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Lee, A. Allen H. Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C. and Seinfeld, J. H.: J. Geophys. Res., 111, D17305, doi:10.1029/2006JD007050, 2006.

Shu, Y. and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

HOx_VOC91: α-copaene

Last evaluated: June 2014; Last change in preferred values: June 2014

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(9.0 \pm 1.9) \times 10^{-11}$	296±2	Shu and Atkinson, 1995	RR (a)

α-Copaene is (1R,2S,6S,7S,8S)-8-isopropyl-1,3-dimethyltricyclo[4.4.0.0^{2,7}]dec-3-ene

Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of CH_3ONO at wavelengths > 300 nm. α-Copaene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, k(HO + α-copaene) / k(HO + 2,3-dimethyl-2-butene) = 0.817 ± 0.044 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	9.0×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Values

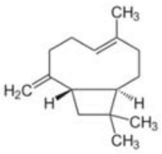
The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995). The reaction is expected to proceed predominantly by addition to the >C=C< double bond.

References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Shu, Y. and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

HOx_VOC92: β-caryophyllene

Last evaluated: June 2014; Last change in preferred values: June 2014

HO + 

→ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.0^{+0.5}_{-0.9}) \times 10^{-10}$	296±2	Shu and Atkinson, 1995	RR (a)

β-caryophyllene is 4,11,11-trimethyl-8-methylene-bicyclo[7.2.0]undec-4-ene

Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of CH_3ONO at wavelengths > 300 nm. β-caryophyllene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. Corrections for the dark decay of β-caryophyllene were made. The rate constant ratio, k(HO + β-caryophyllene) / k(HO + 2,3-dimethyl-2-butene) = 1.79 ± 0.22 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.0×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995).

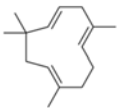
The reaction is expected to proceed predominantly by addition to both the exocyclic and endocyclic double bonds. A large yield (68%) of secondary organic aerosol was reported by Lee et al. (2006) along with gas phase organic species such as HCHO (42±10%), CH_3CHO (0.6±0.2%), HCOOH (6.2±2%), $CH_3C(O)CH_3$ (1.5±0.4%) and $CH_3C(O)OH$ (8.7±2%). Hydroxy-hydroperoxides, dihydroxy compounds and hydroketones are expected to be among the first generation products (Jenkin et al., 2012).

References

Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Jenkin, M. E., Wyche, K. P., Evans, C. J., Carr, T., Monks, P. S., Alfarra, M. R., Barley, M. H., McFiggans, G. B., Young, J. C. and Rickard, A. R.: Atmos. Chem. Phys., 12, 5275–5308, 2012.
Lee, A. Allen H. Goldstein,A. H., Kroll, J. H., Ng, N.L., Varutbangkul, V., Flagan, R. C. and Seinfeld, J. H.: J. Geophys. Res., 111, D17305, doi:10.1029/2006JD007050, 2006
Shu, Y. and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

HOx_VOC93: α-humulene

Last evaluated: June 2014; Last change in preferred values: June 2014

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.9^{+0.7}_{-1}) \times 10^{-10}$	296±2	Shu and Atkinson, 1995	RR (a)

α-Humulene is 2,6,6,9-Tetramethyl-1,4-8-cycloundecatriene

Comments

(a) 6400 L Teflon chamber at 987 mbar (740 Torr) of air. HO radical was generated by the photolysis of CH_3ONO at wavelengths > 300 nm. α-Humulene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC-FID. The rate constant ratio, k(HO + α-humulene) / k(HO + 2,3-dimethyl-2-butene) = 2.66 ± 0.27 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	**Value**	**T/K**
k /cm^3 molecule^{-1} s^{-1}	2.9×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Values

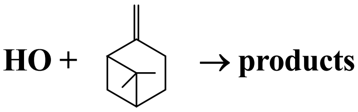
The preferred value of the rate coefficient at 298 K is based on the relative rate coefficient determination of Shu and Atkinson (1995). The reaction is expected to proceed predominantly by addition to the >C=C< double bonds.

References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.
Shu, Y. and Atkinson, R.: J. Geophys. Res., 100, 7275-7281, 1995.

HOx_VOC99: β-pinene

Last evaluated: December 2017; Last change in preferred values: June 2019



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$2.36 \times 10^{-11} \exp[(358 \pm 58)/T]$	297-423	Kleindienst et al., 1982	FP-RF (a)
$(7.76 \pm 1.10) \times 10^{-11}$	297		
$9.96 \times 10^{-12} \exp[(610 \pm 50)/T]$	300-435	Chuong et al., 2002	DF-RF/LIF (b)
$(7.72 \pm 0.44) \times 10^{-11}$	300		
$(7.68 \pm 0.72) \times 10^{-11}$	298	Davis et al. 2005	DF-LIF (c)
Relative Rate Coefficients			
$(6.54 \pm 0.99) \times 10^{-11}$	305 ± 2	Winer et al., 1976	RR/P-GC-FID (d)
$(7.81 \pm 0.51) \times 10^{-11}$	294 ± 1	Atkinson et al., 1986	RR/P-GC-FID (e)
$1.46 \times 10^{-11} \exp[(468 \pm 50)/T]$	295-364	Gill and Hites, 2002	RR/P-MS (f)
$(7.03 \pm 1.60) \times 10^{-11}$	298		
$1.91 \times 10^{-11} \exp[(416 \pm 17)/T]$	240-340	Montenegro et al., 2012	RR/DF-MS (g)
$(7.80 \pm 1.35) \times 10^{-11}$	298		
$(8.72 \pm 2.60) \times 10^{-11}$	298	Dash and Rajakumar, 2013	RR/P-GC-FID (h)

β-pinene is 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane

Comments

(a) Flash photolysis of H_2O/β-pinene mixtures in Ar (buffer gas) at total pressures in the range 50-200 Torr (67-270 mbar) under slow flow conditions. Pseudo-first order decays of HO radical concentrations (monitored by RF) were characterized in the presence of excess concentrations of β-pinene. k displayed no dependence on pressure over the studied range.

(b) Pseudo-first order decays of HO radical concentrations (monitored by RF or LIF) were characterized in the presence of excess concentrations of β-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of either He or 90% He/10% O_2.

(c) Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of β-pinene. Experiments carried out at a total pressure of 5 Torr (6.7 mbar) of mainly He, with O_2 present at ~ 1-4% of the mixture.

(d) HO radicals were generated by the photolysis of NO_x – organic – air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of β-pinene and 2-methylpropene (the reference compound) were analyzed by GC during the experiments. The measured rate coefficient ratio k(HO + β-pinene)/k(HO + 2-methylpropene) = 1.33 (± 30%) is placed on an absolute basis using k(HO + 2-methylpropene) = 4.92×10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (IUPAC, 2019).

(e) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of β-pinene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during UV irradiation of CH_3ONO - NO - β-pinene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio k(HO + β-pinene)/k(HO + 2,3-dimethyl-2-butene) = 0.710 ± 0.046 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.10×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(f) HO radicals were generated by the photolysis of H_2O_2 in helium diluent in a 192 cm^3 volume quartz vessel. The concentrations of β-pinene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS during the experiments. The measured rate coefficient ratios k(HO + β-pinene)/k(HO + 1-butene), k(HO + β-pinene)/k(HO + 2-methylpropene) and k(HO + β-pinene)/k(HO + *trans*-2-butene) are placed placed on an absolute basis using k(HO + 1-butene) = $6.6 \times 10^{-12} \exp(465/T)$ cm^3 $molecule^{-1}$ s^{-1}, k(HO + 2-methylpropene) = $9.4 \times 10^{-12} \exp(505/T)$ cm^3 $molecule^{-1}$ s^{-1} and k(HO + *trans*-2-butene) = $1.0 \times 10^{-11} \exp(553/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

(g) HO radicals were generated by the reaction of H_2O with F atoms (formed from F_2 discharge), and added to flowing mixtures containing β-pinene and isoprene (the reference compound) in helium at a total pressure of 1-8 Torr (1.3-11 mbar). The measured rate coefficient ratios, k(HO + β-pinene)/k(HO + isoprene), are placed on an absolute basis using the rate coefficient expression k(HO + isoprene) = $2.7 \times 10^{-11} \exp(370/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

(h) HO radicals were generated by the photolysis of H_2O_2 in nitrogen diluent at pressures in the range 800 Torr (1070 mbar) in a 1750 cm^3 volume quartz vessel. The concentrations of β-pinene and 2-methylpropene (the reference compound) were analyzed by GC-FID. The measured rate coefficient ratio k(HO + β-pinene)/k(HO + 2-methylpropene) is placed on an absolute basis using k(HO + 2-methylpropene) = 5.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K (IUPAC, 2019).

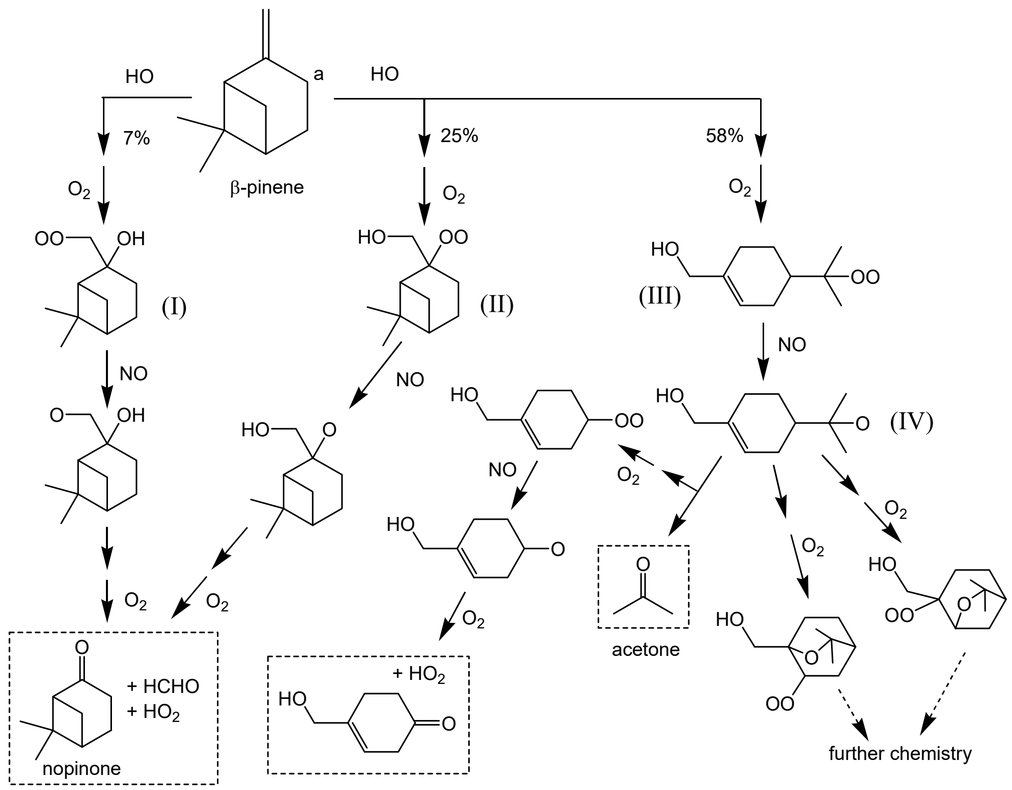
Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	7.6×10^{-11}	298
k /cm^3 $molecule^{-1}$ s^{-1}	$1.62 \times 10^{-11} \exp(460/T)$	240-420
Reliability		
$\Delta \log k$	± 0.05	298
Δ E/R	± 150	240-420

Comments on Preferred Values

The preferred value of E/R is a rounded average of those reported in the four tabulated temperature-dependence studies, with the assigned uncertainty range encompassing the set of values. The 298 K preferred value of k is the average of the room temperature values reported in all the tabulated studies, with those of Winer et al. (1976), Kleindienst et al. (1982), Atkinson et al. (1986) and Choung et al. (2002) corrected to 298 K using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value.

H atom abstraction has been estimated to account for about 10 % of the reaction of HO with β-pinene at 298 K (Vereecken and Peeters, 2012); with position "a" in the schematic below (forming a resonant radical) being the most important attack site. The reaction proceeds mainly by initial addition of the HO radical to the C=C bond, and the schematic illustrates some established and predicted features of the subsequent chemistry in air in the presence of NO_x.



The hydroxy-substituted peroxy radicals, (I), (II) and (III), are formed from sequential addition of HO and O_2, with (III) facilitated by competitive opening of the cyclobutyl ring in the intermediate chemically-activated HO-β-pinene adduct. The approximate contributions of the three pathways shown are based on the calculations of Vereecken and Peeters (2012) for 298 K and 1 bar. The subsequent chemistry, propagated by the reactions of intermediate peroxy radicals with NO, forms a number of carbonyl end products (as shown in boxes). The chemistry of (I) and (II) generates nopinone, which has been reported to be formed with a yield of about 25-30% in experimental studies in the presence of NO_x (Arey et al. 1990; Hakola et al., 1994; Wisthaler et al., 2001). Its co-product, formaldehyde, has been reported to be formed with a higher yield of 45 ± 8 % (Orlando et al., 2000), consistent with its additional formation from other sources in the system. The chemistry of (III) partially generates acetone, which has been reported to be formed in yields in the range 2-13% (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000). Its low yield may be explained by the operation of competing channels for oxy radical intermediate (IV), such as the illustrated ring closure reactions postulated by Vereecken and Peeters (2004; 2012).

The reactions of all the peroxy radicals with NO also partially form the corresponding hydroxy-nitrate products (not shown in the schematic), which have been reported to be formed with a collective yield of about 25% by Ruppert et al. (1999). Other products have also been observed, including formic acid (2%) by Orlando et al. (2000); and product signals consistent with a number of higher molecular weight dihydroxycarbonyl, hydroxynitrate and dihydroxynitrate products by Aschmann et al. (1998).

Other reactions of the intermediate peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low NO_x levels. These include bimolecular reactions with HO_2 and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products. Unimolecular isomerization reactions may also be available for complex peroxy radical intermediates. Vereecken and Peeters (2004) calculated that peroxy radical (III) undergoes a ring closure reaction (forming a peroxide-bridged product) that dominates at ≤ 1 ppb NO; and Berndt et al. (2016) have postulated that auto-oxidation reaction sequences, initiated by isomerization of peroxy radical (III) and involving a number of subsequent peroxy radical isomerization reactions, may account for the observed rapid formation of highly oxidized multifunctional organic compounds from the HO-initiated oxidation of β-pinene in chamber experiments. The role of unimolecular isomerization reactions has recently been confirmed by Xu et al. (2019), who experimentally and theoretically characterized a number of competitive ring-closure and H-atom shift reactions for peroxy radical (III).

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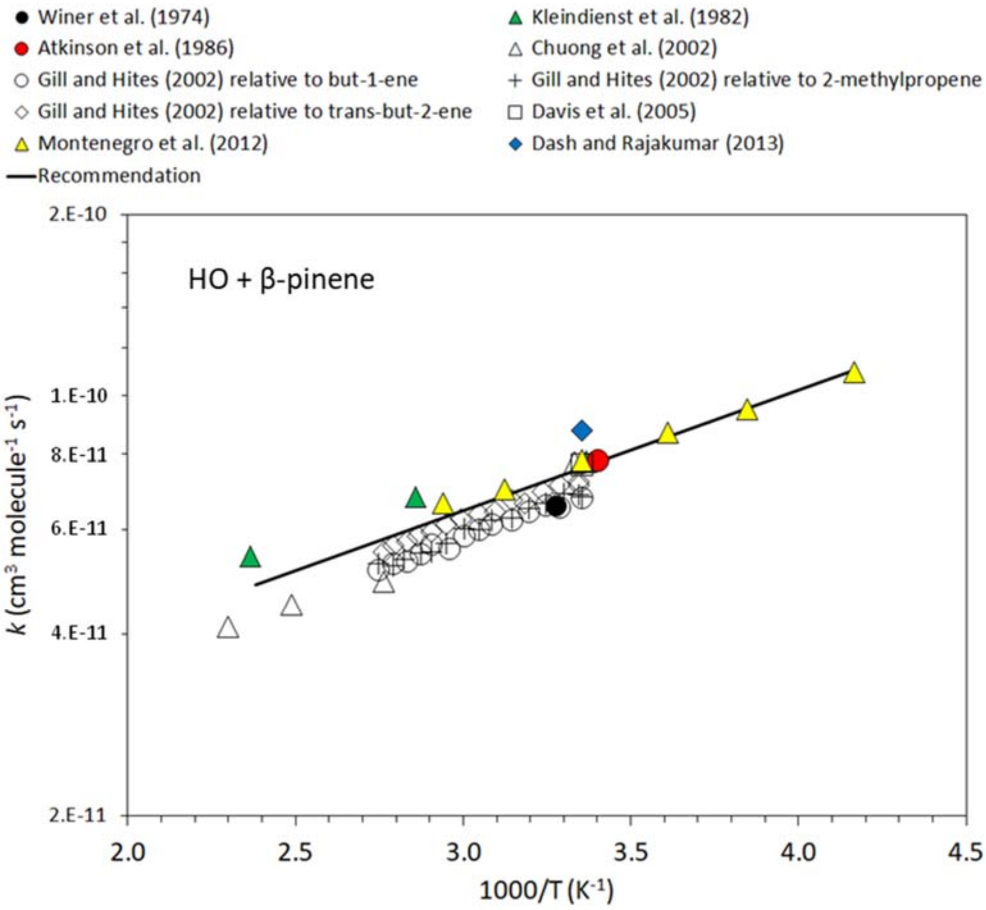
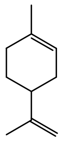


Rate coefficients for HO + β-pinene.

HOx_VOC100: limonene

Last evaluated: December 2017; Last change in preferred values: December 2017

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$4.59 \times 10^{-11} \exp[(382 \pm 154)/T]$	300-360	Braure et al., 2014	DF-MS (a)
1.65×10^{-10}	300		
Relative Rate Coefficients			
$(1.45 \pm 0.22) \times 10^{-10}$	305 ± 2	Winer et al., 1976	RR (b)
$(1.66 \pm 0.50) \times 10^{-10}$	294 ± 1	Atkinson et al., 1986	RR (c)
$4.20 \times 10^{-11} \exp[(401 \pm 43)/T]$	295-364	Gill and Hites, 2002	RR (d)
$(1.61 \pm 0.31) \times 10^{-10}$	298		
$2.53 \times 10^{-11} \exp[(569 \pm 56)/T]$	220-355	Braure et al., 2014	DF-MS (a)
1.70×10^{-10}	298*		

limonene is 4-isopropenyl-1-methyl-cyclohexene

*) the experimental temperature was “room temperature” which we list as 298K.

Comments

(a) Both absolute and relative rate determinations reported, carried out in 1 Torr (1.3 mbar) of He. Absolute rate coefficients determined mainly from observed decay of HO concentration in excess limonene, but with some experiments monitoring the decay of limonene concentration in excess HO. k was also reported to be independent of pressure over the range 0.5-5 Torr (0.7-6.7 mbar). Relative rate determinations carried out using either the HO + CH_3SSCH_3 reaction or the HO + Br_2 reaction as a reference, with the latter monitored using the formation of the product HOBr. The measured rate coefficient ratios k(HO + limonene)/k(HO + CH_3SSCH_3) and k(HO + limonene)/k(HO + Br_2) are placed on an absolute basis using k(HO + CH_3SSCH_3) = $7.0 \times 10^{-11} \exp(350/T)$ cm^3 molecule^{-1} s^{-1} and k(HO + Br_2) = $1.9 \times 10^{-11} \exp(240/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019). The authors preferred to report a rate expression based on a combined analysis of all data. Applying the above reference rate coefficients, this results in the slightly adjusted expression, $k = 2.8 \times 10^{-11} \exp(543/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 220-360 K, which is used here to represent their data. Almost identical temperature-dependent rate coefficients were also reported for the DO + limonene reaction, with the branching ratio for H atom abstraction described by $(0.07 \pm 0.03) \exp((460 \pm 140)/T)$ over the temperature range 253-355K, based on monitoring the formation of HDO.

(b) HO radicals were generated by the photolysis of NO_x - organic - air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of limonene and 2-methylpropene (the reference compound) were analyzed by GC. The measured rate coefficient ratio k(HO + limonene)/k(HO + 2-methylpropene) is placed on an absolute basis using k(HO + 2-methylpropene) = 4.92×10^{-11} cm^3 molecule^{-1} s^{-1} at 305 K (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of limonene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during UV irradiation of CH_3ONO - NO - limonene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio *k*(HO + limonene)/*k*(HO + 2,3-dimethyl-2-butene) = 1.51 ± 0.04 is placed on an absolute basis using *k*(HO + 2,3-dimethyl-2-butene) = 1.10×10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(d) HO radicals were generated by the photolysis of H_2O_2 in helium diluent in a 192 cm^3 volume quartz vessel. The concentrations of limonene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS. The measured rate coefficient ratios *k*(HO + limonene)/*k*(HO + 1-butene), *k*(HO + limonene)/*k*(HO + 2-methylpropene) and *k*(HO + limonene)/*k*(HO + *trans*-2-butene) are placed on an absolute basis using *k*(HO + 1-butene) = $6.6 \times 10^{-12} \exp(465/T)$ cm^3 $molecule^{-1}$ s^{-1}, *k*(HO + 2-methylpropene) = $9.4 \times 10^{-12} \exp(505/T)$ cm^3 $molecule^{-1}$ s^{-1} and *k*(HO + *trans*-2-butene) = $1.0 \times 10^{-11} \exp(553/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

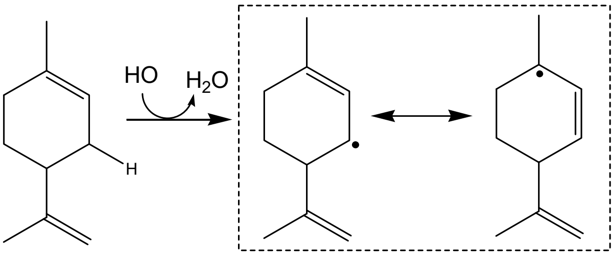
Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	1.65×10^{-10}	298
k /cm^3 $molecule^{-1}$ s^{-1}	$3.41 \times 10^{-11} \exp(470/T)$	220-360
Reliability		
$\Delta \log k$	± 0.05	298
Δ E/R	± 150	220-360

Comments on Preferred Values

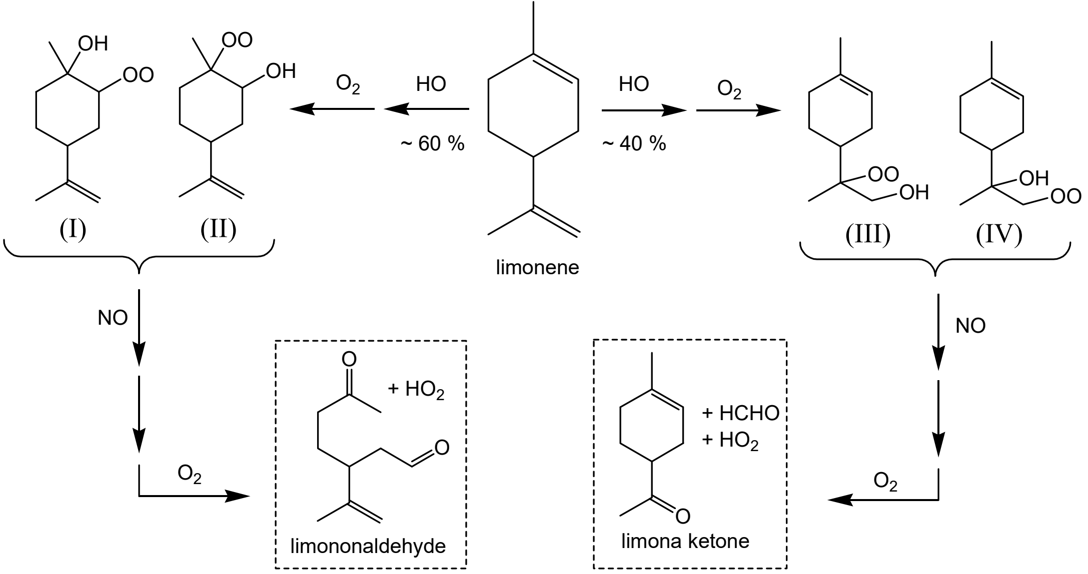
The preferred value of *E*/*R* is a rounded average of the values of Gill and Hites (2002) and Braure et al. (2014), with the latter based on the composite analysis of all their data (see comment (a)). The 298 K preferred value of *k* is the average of the room temperature values reported by Atkinson et al. (1986), corrected to 298 K using the preferred temperature dependence, Gill and Hites (2002) and Braure et al. (2014), based on the composite analysis of all their data (see comment (a)), which are in good agreement. The determination of Winer et al. (1974) is about 10 % lower than the preferred value, but within the assigned uncertainty bounds. The pre-exponential factor is adjusted to fit the 298 K preferred value.

H-atom abstraction has been reported to account for about 30 % of the reaction of HO (or DO) with limonene at 298 K (Rio et al., 2010; Braure et al., 2014). Rio et al. (2010) derived their value from analysis of the time-dependence of composite product peroxy radical absorptions (UV absorption) in air at atmospheric pressure, and from observation of product radical fragments (MS) at low pressure in the absence of O_2. Braure et al. (2014) derived their value from formation of HDO from the reaction of DO with limonene. They also observed an unexpected negative temperature dependence in the branching ratio (see comment (a)), suggesting a contribution of H-atom abstraction of over 40% at 250 K. A significant contribution of H-atom abstraction is expected to be facilitated by formation of resonant product radicals, following abstraction at five of the six available (saturated carbon) sites, e.g.:



However, theoretical (Dash and Rajakumar, 2015) and structure activity methods (Vereecken and Peeters, 2001), predict a much lower contribution of about 3-17 % from H-atom abstraction at 298 K, and a positive temperature dependence. Confirmatory experimental and theoretical studies would therefore be valuable.

HO addition is expected to occur significantly at both the endocyclic and exocyclic double bonds in limonene, and the schematic below illustrates some established features of the subsequent chemistry in air in the presence of NO_x.



The hydroxy-substituted peroxy radicals, (I) and (II), are formed from sequential addition of HO and O_2 to the endocyclic bond, and (III) and (IV) are formed from addition to the exocyclic bond; with the approximate addition contributions shown based on structure activity methods (Peeters et al., 2007). The subsequent chemistry, propagated by the reactions of intermediate peroxy radicals with NO, forms a number of carbonyl end products (as shown in boxes). The chemistry of (I) and (II) generates limononaldehyde (3-isopropenyl-6-oxo-heptanal), for which yields of 28 % and 29 ± 6 % in the presence of NO_x have been reported by Arey et al. (1990) and Hakola et al. (1994) respectively. The chemistry of (III) and (IV) generates limona ketone (4-acetyl-1-methyl-cyclohexene), for which the reported yields are 17.4 ± 2.8 % (Arey et al., 1990) and 20 ± 3 % (Hakola et al., 1994). Its co-product, formaldehyde, has been reported to be formed with a yield of 43 ± 5 % in photo-oxidation experiments (Lee et al., 2006), although limonene was partially reacting with O_3 under their experimental conditions. The reactions of all the peroxy radicals with NO also partially form the corresponding hydroxy-nitrate products (not shown in the schematic), which have been reported to be formed with a collective yield of about 23% by Ruppert et al. (1999).

Other reactions of the intermediate peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low NO_x levels. These include bimolecular reactions with HO_2 and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products.

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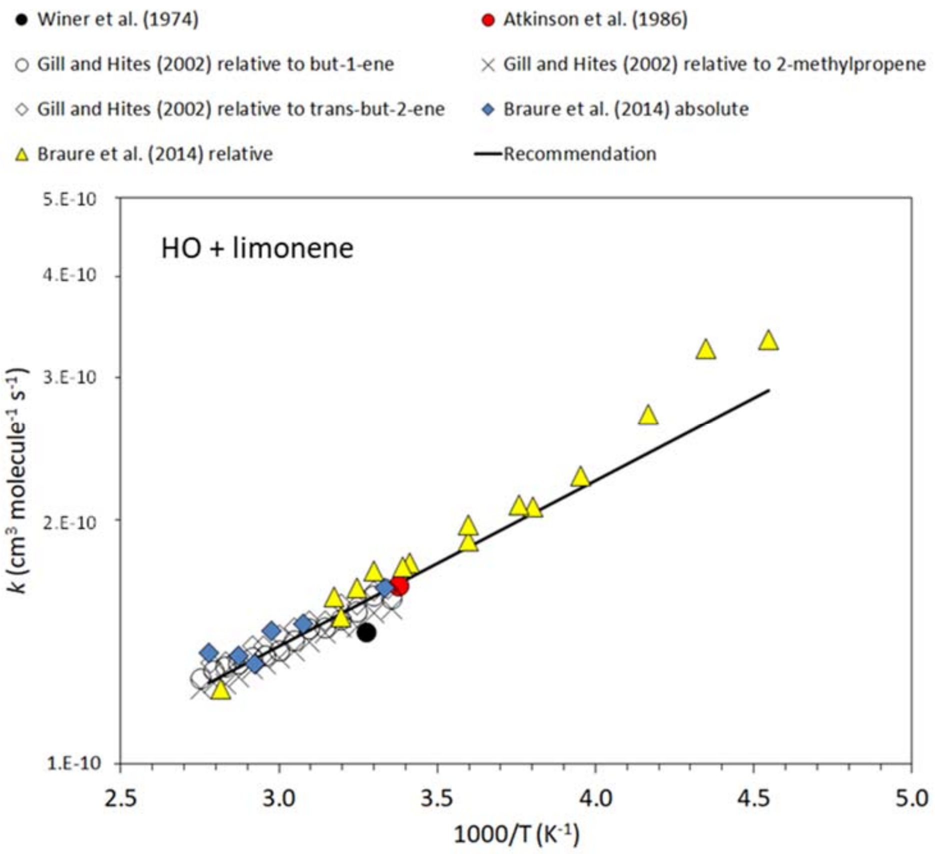

Rate coefficients for HO + limonene.

HOx_VOC101: camphene

Last evaluated: June 2019; Last change in preferred values: June 2019

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(5.28 \pm 0.20) \times 10^{-11}$	296 ± 2	Atkinson et al., 1990	RR-GC-FID (a)
$4.1\times10^{-12}\exp[(754\pm44)/T]$	288-311	Gaona-Colman et al., 2017	RR-FTIR (b, c)
$(5.1 \pm 1.1) \times 10^{-11}$	298	Gaona-Colman et al., 2017	(b, c)
$(5.1 \pm 0.3) \times 10^{-11}$	298	Gaona-Colman et al., 2017	(b, d)

Camphene is 2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane.

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of camphene and isoprene (the reference compound) were analyzed by GC-FID during UV irradiation of CH_3ONO - NO - camphene - isoprene - air mixtures. The measured rate coefficient ratio k(HO + camphene)/k(HO + isoprene) = 0.528 ± 0.019 is placed on an absolute basis using k(HO + isoprene) = 1.0×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of H_2O_2 in nitrogen at 254 nm in a 1080 L Teflon chamber at ~1000 mbar pressure. The concentrations of camphene and isoprene (the reference compound) were analyzed by long path FTIR during UV irradiation of H_2O_2 - camphene - reference - nitrogen mixtures. Two references were employed, 2,3-dimethyl-2-butene and isobutene at 298 K and isobutene in the temperature range 288-311 K. The measured rate coefficient ratios, k(HO + camphene)/k(HO + 2,3-dimethyl-2-butene) = 0.47 ± 0.01 and k(HO + camphene)/k(HO + isobutene) = 0.99 ± 0.02 are placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.09×10^{-10} cm^3 molecule^{-1} s^{-1} (Atkinson et al., 1983) and k(HO + isobutene) = 5.14×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson, 1997). The measured rate coefficients in the temperature range 288-311 K are placed on an absolute basis using k(HO + isobutene) = $9.47 \times 10^{-12} \exp(504/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997).

(c) Relative to isobutene.

(d) Relative to 2,3-dimethyl-2-butene.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	5.2×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$4.14 \times 10^{-12} \exp(754/T)$	280-320
Reliability		
$\Delta \log k$	± 0.10	298

Δ E/R	± 100	280-320

Comments on Preferred Values

The 298 K rate coefficients values from the absolute and relative studies of Gaona-Colman et al. (2017) are in very good agreement with the relative determination of Atkinson et al. (1990). Fitting the Arrhenius expression to the data from Gaona-Colman et al. (2017) and adjusting the A-factor slightly to reproduce the recommended value at 298 K gives the preferred temperature dependence expression.

The reaction of OH radical with camphene proceeds mainly by addition of OH to the double bond terminal carbon atom to form hydroxylalkyl radicals that will add O_2 to form hydroxyalkylperoxy radicals. In the presence of NO, hydroxyalkylperoxy radicals will be converted to hydroxyalkoxy radicals, which may either decompose or react with O_2. In absence of NOx, hydroxyalkylperoxy radicals undergo self-reaction and reactions with other peroxy radicals. Reissell et al (1999) and Gaona-Colman et al. (2017) have reported, respectively, (39±5)% and (33±6)% formation yields of acetone in presence of NOx. In absence of NOx, the yield of acetone reported by Gaona-Colman et al. (2017) was (10±2)%. The formaldehyde yields obtained by Gaona-Colman et al. (2017) were (3.6±0.7)% and (10±2)% in the absence and presence of NOx, respectively. Hakola et al. (1994) have observed the formation of camphenilone (3,3-dimethylbicyclo[2.2.1]heptan-2-one) and 6,6-dimethyl-3-caprolactone-2,5-methylene (4,4-dimethyl-3-oxabicyclo[3.2.1]octan-2-one) with very small yields (<0.02%).

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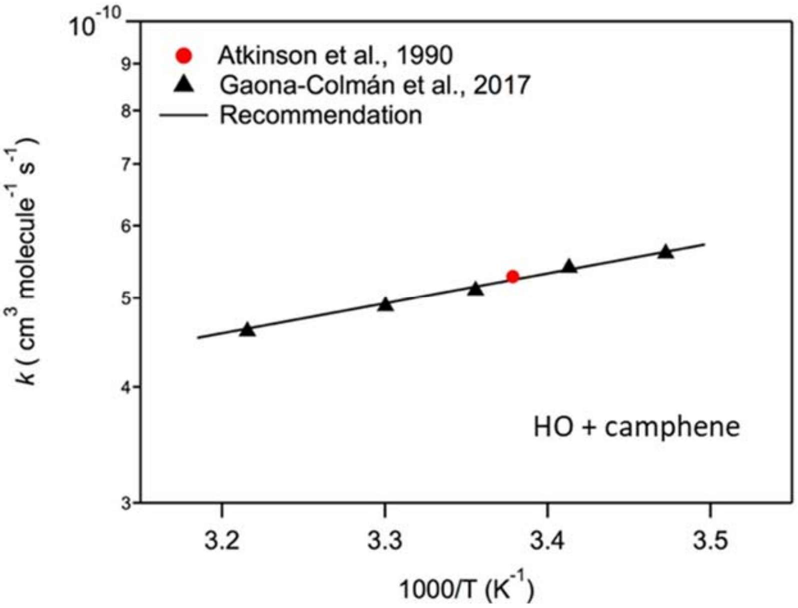
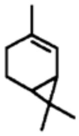
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J, Geophys. Res., 104, 13869, 1999.



Rate coefficients for HO + camphene.

HOx_VOC102: 2-carene

Last evaluated: June 2019; Last change in preferred values: June 2019

HO +  → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
(7.95 ± 2.00) × 10^{-11}	295 ± 2	Corchnoy and Atkinson, 1990	RR-GC-FID (a)

2-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-2-ene.

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of 2-carene and isoprene (the reference compound) were analyzed by GC-FID during UV irradiation of CH_3ONO - NO - 2-carene - isoprene - air mixtures. The measured rate coefficient ratio k(HO + camphene)/k(HO + isoprene) = 0.779 ± 0.023 is placed on an absolute basis using k(HO + isoprene) = 1.0 × 10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	8.0 × 10^{-11}	298
Reliability		
Δ log k	± 0.15	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Corchnoy and Atkinson (1990). The error limits have been expanded to reflect the fact that this is the only study available. The reaction is expected to proceed predominantly by addition to the >C=C< double bond.

References

Corchnoy, S. B. and Atkinson, R.: Environ. Sci. Technol. 24, 1497, 1990.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_VOC103: 3-carene

Last evaluated: June 2019; Last change in preferred values: June 2019

HO +

→ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
2.48×10^{-11} exp[$(357 \pm 17)/T$]	235-357	Dillon et al., 2017	PLP-LIF (a)
$(8.1 \pm 0.3) \times 10^{-11}$	297		
Relative Rate Coefficients			
$(8.55 \pm 0.42) \times 10^{-11}$	294 ± 1	Atkinson et al., 1986	RR-GC-FID (b)

2-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-2-ene.

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 at 248 nm in the presence of 3–carene/N_2 or 3-carene /air mixtures at total pressures in the range 9-281 mbar (7-211 Torr) and their concentration measured by pulsed laser induced fluorescence. Pseudo-first order decays of HO radical concentrations were characterized in the presence of excess concentrations of 3-carene (monitored by vacuum UV optical absorption at 185 nm). The rate constants were independent of the bath-gas pressure over the studied range or type (N_2 or air). The reported value is the mean of the results obtained under different conditions (pressure and bath-gas).

(b) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of 3-carene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC-FID during UV irradiation of CH_3ONO - NO - 3-carene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio k(HO + 3-carene)/k(HO + 2,3-dimethyl-2-butene) = 0.777 ± 0.038 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.10×10^{-10} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	8.3×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	2.5×10^{-11} exp($357/T$)	230-360
Reliability		
$\Delta \log k$	± 0.06	298

Δ E/R	± 50	230-360

Comments on Preferred Values

The room temperature values of *k* in the reported studies are in agreement. The preferred rate coefficient value at 298 K is derived from the average of the two measurements. The absolute rate study of Dillon et al. (2017), the sole temperature-dependence study, combined with the preferred 298 K is used to derive the pre-exponential factor. The reaction is expected to proceed predominantly by addition to the >C=C< double bond. Reissell et al. (1999) have reported an acetone formation yield of (15±3)% in the presence of NO while Hakola et al. (1994) have identified 2,2-dimethyl-3-(2-oxopropyl)-cyclopropaneacetaldehyde with a yield of (34±8)%.

References

Atkinson, R., Aschmann, S. M. and Pitts Jr. J. M.: Int. J. Chem. Kinet., 18, 287, 1986.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
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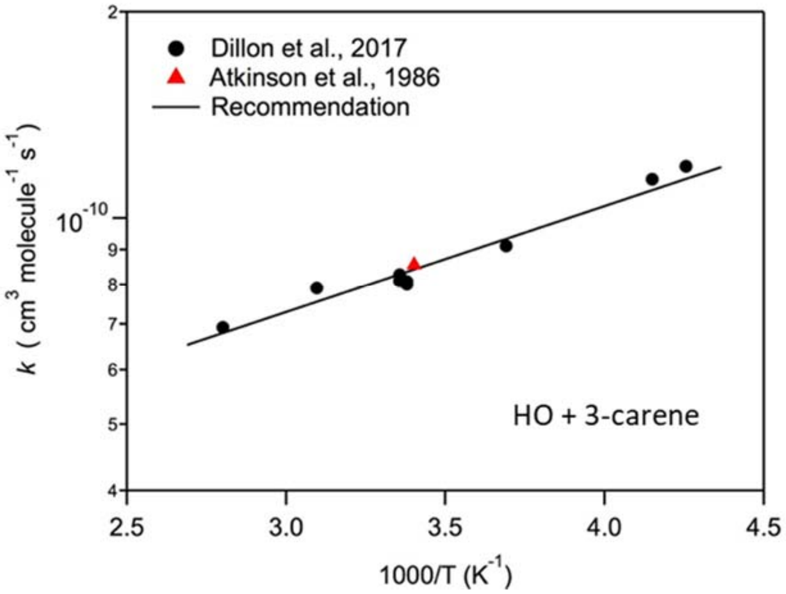


Rate coefficients for HO + 3-carene.

HOx_VOC104: β-myrcene

Last evaluated: June 2019; Last change in preferred values: June 2019

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.09 \pm 0.16) \times 10^{-10}$	294 ± 1	Atkinson et al., 1986	RR-GC-FID (a)
$9.19 \times 10^{-12} \exp[(1071 \pm 82)/T]$	313-423	Hites and Turner, 2009	RR-MS (b)

Myrcene is 7-methyl-3-methylene-1,6-octadiene.

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of β-myrcene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC-FID during UV irradiation of CH_3ONO - NO - β-myrcene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio k(HO + β-myrcene)/k(HO + 2,3-dimethyl-2-butene) = 1.90 ± 0.14 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.10×10^{-10} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) HO radicals were generated by the photolysis of H_2O_2 in helium at wavelengths <360 nm in a 160 cm^3 volume quartz vessel at ~1 bar pressure. The concentrations of β-myrcene and isoprene (the reference compound) were monitored by MS. The measured rate coefficient ratios, k(HO + β-myrcene)/k(HO + isoprene), were placed on an absolute basis using k(HO + isoprene) = $3.14\times10^{-17}\ T^2 \times \exp(1036/T)$ cm^3 molecule^{-1} s^{-1} (Hites and Turner, 2009), which agrees with the IUPAC recommendation over the studied temperature range (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.1×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.15	298

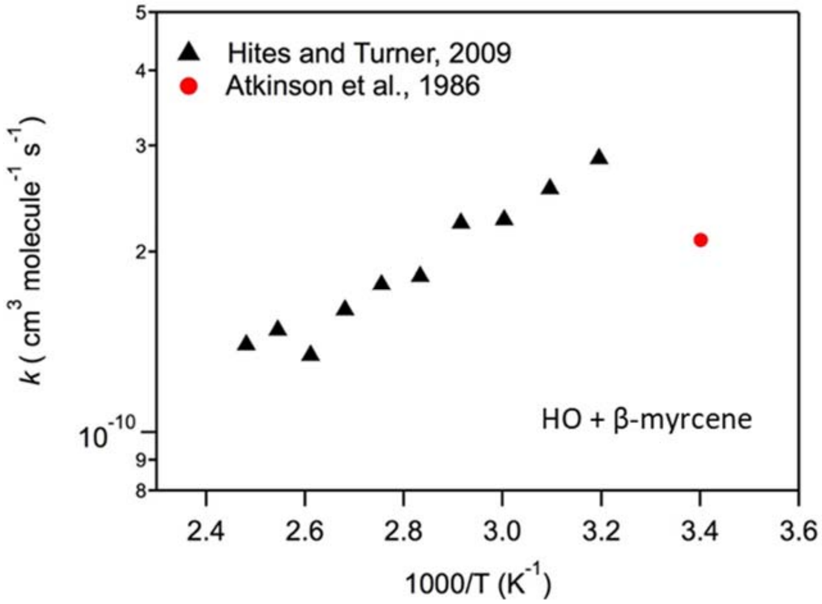
Comments on Preferred Values

The preferred rate coefficient value at 298 K is based on the relative rate measurement from Atkinson et al. (1986). Hites and Turner have not measured the rate coefficient at room temperature. An extrapolation of their data to room temperature using their Arrhenius expression leads to $k_{298} = 3.3\times10^{-10}$ cm^3 molecule^{-1} s^{-1} which is ≈ 50 % higher than that reported by Atkinson et al. (1986). Hites and Turner mentioned some possible experimental difficulties in deriving their values. Hence, no recommendation is made for the temperature dependence expression.

The reaction is expected to proceed predominantly by addition to the >C=C< double bonds. Reissell et al. (1999) have reported an acetone formation yield of (45±6)% in the presence of NO indicating that at least that fraction of the reaction occurs via addition of OH to $>C=C(CH_3)_2$.

References

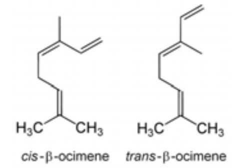
Atkinson, R., Aschmann, S. M. and Pitts Jr., J. M.: Int. J. Chem. Kinet., 18, 287, 1986.
Hites, R. A. and Turner, A. M.: Int. J. Chem. Kinet., 41, 407, 2009.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.



Rate coefficients for HO + β-myrcene.

HOx_VOC105: *cis-/trans-*ocimene

Last evaluated: June 2019; Last change in preferred values: June 2019

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.45 \pm 0.19) \times 10^{-10}$	294 ± 1	Atkinson et al., 1986	RR-GC-FID (a)
$4.35 \times 10^{-11} \exp[(579 \pm 59)/T]$	313-423	Kim et al., 2011	RR-MS (b)

Ocimene is 3,7-dimethyl-1,3,6-octatriene.

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of β-ocimene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC-FID during UV irradiation of CH_3ONO - NO - β-ocimene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio k(HO + β-ocimene)/k(HO + 2,3-dimethyl-2-butene) = 2.23 ± 0.17 is placed on an absolute basis using k(HO + 2,3-dimethyl-2-butene) = 1.10×10^{-10} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) HO radicals were generated by the photolysis of H_2O_2 in helium at wavelengths <360 nm in a 160 cm^3 volume quartz vessel at ~1 bar pressure. The concentrations of β-ocimene and 2-methylpropene (the reference compound) were monitored by MS. The measured rate coefficient ratios, k(HO + β-ocimene)/k(HO + 2-methylpropene), were placed on an absolute basis using k(HO + 2-methylpropene) = $0.947 \times 10^{-11} \times \exp(504/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.8×10^{-10}	298
k /cm^3 molecule^{-1} s^{-1}	$4.0 \times 10^{-11} \exp(579/T)$	310-430
Reliability		
Δ log k	± 0.15	298
Δ E/R	± 150	310-430

Comments on Preferred Values

An extrapolation of the data from Kim et al. (2011) at 298K using their Arrhenius expression leads to $k_{298} = 3.04\times10^{-10}$ cm^3 molecule^{-1} s^{-1} which is ≈ 20 % higher than that reported by Atkinson et al. (1986). The preferred rate coefficient value at 298 K is the average of the measurement from Atkinson et al. (1986) and that from Kim et al. (2011) extrapolated to 298K. The study of Kim et al. (2011), the sole temperature-dependence study, combined with the preferred 298 K is used to derive the pre-exponential factor.

The reaction is expected to proceed predominantly by addition to the >C=C< double bonds. Reissell et al. (1999) have reported an acetone formation yield of (20±15)% in the presence of NO indicating that at least that fraction of the overall reaction occurs via addition of OH to $>C=C(CH_3)_2$.

References

Atkinson, R., Aschmann, S. M., Pitts, Jr. J. M.: Int. J. Chem. Kinet., 18, 287, 1986.

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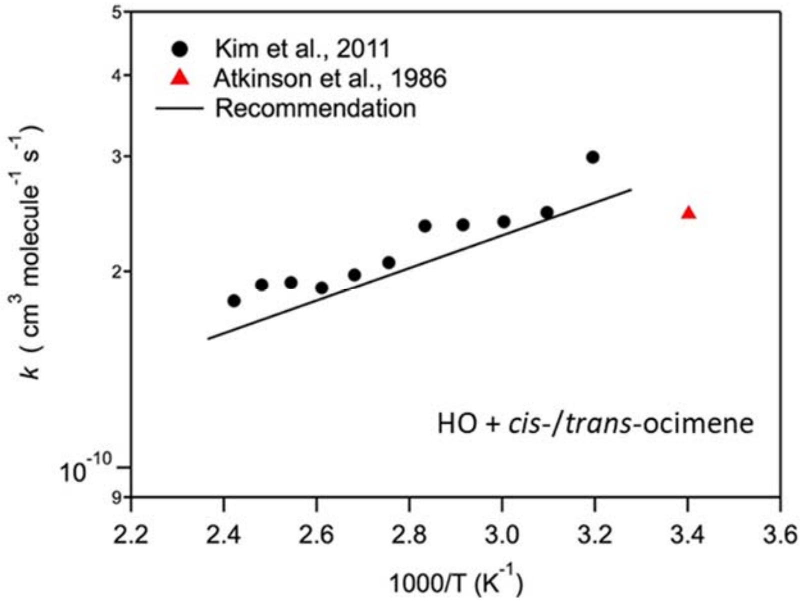
Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.



Rate coefficients for HO + *cis*-/*trans*-ocimene.

HOx_VOC106: sabinene

Last evaluated: June 2019; Last change in preferred values: June 2019

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.16\pm 0.05)\times 10^{-10}$	296 ± 2	Atkinson et al., 1990	RR-GC-FID (a)

Sabinene is 1-isopropyl-4-methylene-bicyclo[3.1.0]hexane.

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of camphene and isoprene (the reference compound) were analyzed by GC-FID during UV irradiation of CH_3ONO - NO - sabinene - isoprene - air mixtures. The measured rate coefficient ratio k(HO + sabinene)/k(HO + isoprene) = 1.16 ± 0.04 is placed on an absolute basis using k(HO + isoprene) = 1.0×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.2×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the single study of Atkinson et al. (1990). The error limits are expanded to reflect the single measurement.

The reaction is expected to proceed mainly by addition of OH to the CH_2=C< bond with a non-negligible contribution from H-atom abstraction. Reissell et al. (1999) have reported (19±0.3)% formation yield of acetone in presence of NOx. Hakola et al. (1994) have observed the formation of sabinaketone with a yield of 7.3 %.

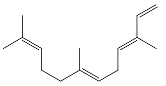
References

Atkinson, R., Aschmann, S. M. and Arey, J.: Atmos. Environ., 24, 2647, 1990.
Hakola, H., Arey, J., Aschmann, S. M. and Atkinson, R.: J. Atmos. Chem., 18, 75, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Reissell, A., Harry, C., Aschmann, S. M., Atkinson, R. and Arey, J.: J. Geophys. Res., 104, 13869, 1999.

HOx_VOC107: α-farnesene

Last evaluated: December 2017; Last change in preferred values: December 2017

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.19 \pm 0.11) \times 10^{-10}$	313-423	Kim et al., 2011	RR-MS (a)

α-farnesene is 3,7,11-trimethyl-dodeca-1,3,6,10-tetraene

Comments

(a) The concentrations of α-farnesene and 2-methylpropene (the reference compound) were monitored by MS during UV photolysis of H_2O_2 - α-farnesene - 2-methylpropene - He mixtures in a 160 cm^3 volume quartz vessel at ~1 bar pressure. The measured rate coefficient ratios, k(HO + α-farnesene)/k(HO + 2-methylpropene), were placed on an absolute basis using k(HO + 2-methylpropene) = $9.47 \times 10^{-12} \exp(504/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997), which agrees with the current IUPAC recommendation to within 0.5 % over the studied temperature range (IUPAC, 2019). The resultant values of k displayed no significant temperature dependence, and the reported rate coefficient was based on the mean of the measured values.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.2×10^{-10}	298
k /cm^3 molecule^{-1} s^{-1}	2.2×10^{-10}	298-430
Reliability		
$\Delta \log k$	± 0.30	298
$\Delta E/R$	± 200	298-430

Comments on Preferred Values

The preferred temperature-independent value of k is based on the determination of Kim et al. (2011), with the lower bound of the temperature range extended to 298 K. This is the only reported investigation of the reaction, and confirmatory studies are required.

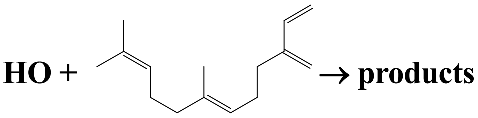
There have been no reported product or mechanistic investigations, and such studies are also required. However, structure-activity methods (e.g. Vereecken and Peeters, 2001; Peeters et al., 2007) suggest that the reaction should proceed mainly by addition of HO to the C=C bonds (with contributions from all sites); but with a non-negligible contribution from H-atom abstraction, which results in formation of resonance-stabilized allyl and superallyl radicals from attack at all (saturated carbon) sites.

References

Atkinson, R.: Phys. Chem. Ref. Data, 26, 215, 1997.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Kim, D., Stevens, P. S. and Hites, R. A.: J. Phys. Chem. A, 115, 500, 2011.
Peeters, J., Boullart, W., Pultau, V., Vandenberk, S. and Vereecken, L.: J. Phys. Chem. A, 111, 1618, 2007.
Vereecken, L. and Peeters, J.: Chem. Phys. Lett., 333, 162, 2001.

HOx_VOC108: β- farnesene

Last evaluated: December 2017; Last change in preferred values: December 2017



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Technique/Comments
Relative Rate Coefficients			
$(2.88 \pm 0.15) \times 10^{-10}$	313-423	Kim et al., 2011	RR-MS (a)
$(1.74 \pm 0.09) \times 10^{-10}$	296 ± 2	Kourtchev et al., 2012	RR-FTIR (b),(c)
$(1.61 \pm 0.18) \times 10^{-10}$	296 ± 2	Kourtchev et al., 2012	RR-FTIR (b),(d)

β-farnesene is (6E)-7,11-dimethyl-3-methylene-1,6,10-dodecatriene

Comments

(a) The concentrations of β-farnesene and 2-methylpropene (the reference compound) were monitored by MS during UV photolysis of H_2O_2 - β-farnesene - 2-methylpropene - He mixtures in a 160 cm^3 volume quartz vessel at ~1 bar pressure. The measured rate coefficient ratios, k(HO + β-farnesene)/k(HO + 2-methylpropene), were placed on an absolute basis using k(HO + 2-methylpropene) = $9.47 \times 10^{-12} \exp(504/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997), which agrees with the current IUPAC recommendation to within 0.5 % over the studied temperature range (IUPAC, 2019). The resultant values of k displayed no significant temperature dependence, and the reported rate coefficient was based on the mean of the measured values.

(b) The concentrations of *trans*-β-farnesene and cyclohexa-1,3-diene or α-terpinene (the reference compounds), were monitored by long path FTIR during UV photolysis of H_2O_2 - *trans*-β-farnesene - reference compound mixtures in a 3.91 m^3 FEP chamber at 0.1–1 mbar above atmospheric pressure of purified air. The measured rate coefficient ratios, k(HO + *trans*-β-farnesene)/k(HO + cyclohexa-1,3-diene) = (1.06 ± 0.04) and k(HO + *trans*-β-farnesene)/k(HO + α-terpinene) = (0.46 ± 0.01), are placed on an absolute basis using k(HO + cyclohexa-1,3-diene) = 1.64×10^{-10} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) and k(O_3 + α-terpinene) = 3.5×10^{-10} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019)) at 296 K. Gas phase carbonyl products were also identified, following photolysis of HONO - *trans*-β-farnesene - air mixtures, as O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine derivatives (GC-MS), by collection on denuders.

(c) Relative to cyclohexa-1,3-diene.

(d) Relative to α-terpinene.

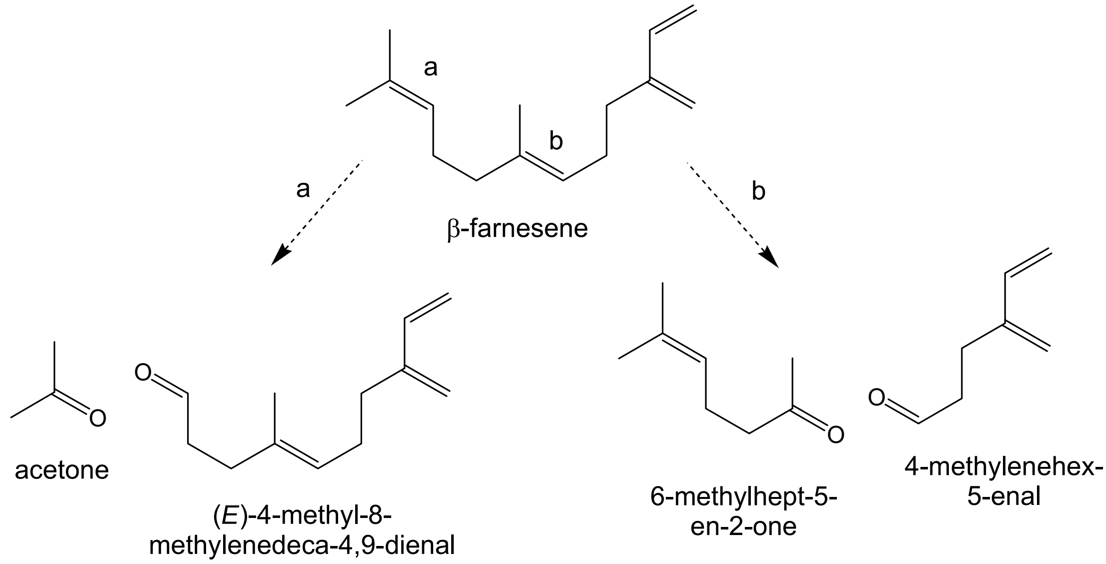
Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.3×10^{-10}	298
k /cm^3 molecule^{-1} s^{-1}	2.3×10^{-10}	296-430
Reliability		
$\Delta \log k$	± 0.30	298
Δ E/R	± 200	296-430

Comments on Preferred Values

The preferred value of *k* is the average of the temperature-independent determination of Kim et al. (2011) and the room temperature determination of Kourtchev et al. (2012) (based on the mean of their two values), recommended for the temperature range 296-430 K. The reported values in the two studies differ by a factor of 1.7, and this is reflected in the assigned uncertainty. Additional studies are required to reduce this uncertainty.

Structure-activity methods (e.g. Vereecken and Peeters, 2001; Peeters et al., 2007) predict that the reaction should proceed mainly by addition of HO to the C=C bonds; but with a non-negligible contribution from H-atom abstraction, which results in formation of resonance-stabilized allyl radicals from attack at all (saturated carbon) sites. Kourtchev et al. (2012) reported evidence for HO addition to the two isolated C=C bonds (“a” and “b”), through detection of the corresponding carbonyl end products (acetone, (*E*)-4-methyl-8-methylenedeca-4,9-dienal, 4-methylenehex-5-enal and 6-methylhept-5-en-2-one), shown in the schematic below:



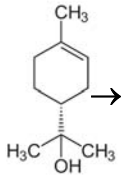
As presented by Kourtchev et al. (2012), these can be formed from the NO-catalyzed chemistry via intermediate β-hydroxy peroxy and oxy radical intermediates. They also reported detection of 4-oxopentanal, which may be formed from secondary oxidation of both (*E*)-4-methyl-8-methylenedeca-4,9-dienal and 6-methylhept-5-en-2-one. Addition of HO to the conjugated diene system is expected to be significant, although no evidence has been reported for the likely carbonyl end products (e.g. 6,10-dimethyl-2-methylene-undeca-5,9-dienal, 7,11-dimethyl-dodeca-1,6,10-trien-3-one and formaldehyde). Similarly, a significant contribution from H-atom abstraction chemistry also requires experimental confirmation.

References

Atkinson, R.: Phys. Chem. Ref. Data, 26, 215, 1997.
Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Kim, D., Stevens, P. S. and Hites, R. A.: J. Phys. Chem. A, 115, 500, 2011.
Kourtchev, I., Bejan, I, Sodeau, J. R. and Wenger, J. C: Atmos. Environ., 46, 338, 2012.
Peeters, J., Boullart, W., Pultau, V., Vandenberk, S. and Vereecken, L.: J. Phys. Chem. A, 111, 1618, 2007.
Vereecken, L. and Peeters, J.: Chem. Phys. Lett., 333, 162, 2001.

HOx_VOC109: α-terpineol

Last evaluated: June 2019; Last change in preferred values: June 2019

HO +  → **products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.9 \pm 0.5) \times 10^{-10}$	297 ± 3	Wells, 2005	RR/GC-MS (a)

α-terpineol is: (2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol.

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air at wavelengths >300 nm in 60-100 L Teflon chamber in air at ~980 mbar pressure. Relative rate of loss of α-terpineol and either 2,5-dimethyl furan and isoprene was monitored by GC-MS. k(α-terpineol) / k(reference), not provided by the authors, was put on an absolute basis using k(isoprene) = 1.01×10^{-10} and k(2,5-dimethyl furan) = 1.32×10^{-10} cm^3 molecule^{-1} s^{-1} (Bierbach et al., 1992).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.9×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.30	298

Comments on Preferred Values

The preferred value at 298 K is an averge of the results from the relative rate studies of Wells (2005). The error limits have been expanded to reflect the fact that this is the only study available.

Wells (2005) positively identified acetone ($CH_3C(O)CH_3$), glyoxal ($HC(O)C(O)H$) and methylglyoxal ($CH_3C(O)C(O)H$) as the products of the reaction between HO and α-terpineol, concluding that both addition of HO to the double bond as well as abstraction of H-atom take place. Yields were not reported. Other products have been observed but not positively identified.

References

Bierbach, A., Barnes, I. and Becker, K. H.: Atmos. Env. 26, 813, 1992.
Wells, J. R. : Environ. Sci. Technol., 39, 6937, 2005.

HOx_AROM1: benzene

Last evaluated: August 2008; Last change in preferred values: August 2008

$$\mathrm{HO} + \mathrm{C_6H_6} \rightarrow \mathrm{H_2O} + \mathrm{C_6H_5} \quad (1)$$
$$\rightarrow \mathrm{HOC_6H_6} \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.59 \pm 0.12) \times 10^{-12}$	298	Davis et al., 1975	FP-RF (a)
$(1.24 \pm 0.12) \times 10^{-12}$	298	Hansen et al., 1975	FP-RF (b)
$(1.20 \pm 0.15) \times 10^{-12}$	297.6	Perry et al., 1977	FP-RF (c)
$(1.32 \pm 0.30) \times 10^{-12}$	304.4		
$(1.33 \pm 0.25) \times 10^{-12}$	305.8		
$(1.66 \pm 0.25) \times 10^{-12}$	322.7		
$(2.6 \pm 1.5) \times 10^{-13}$	396.2		
$(3.4 \pm 0.7) \times 10^{-13}$	396.4		
$(3.4 \pm 1.2) \times 10^{-13}$	405.8		
$(4.5 \pm 0.7) \times 10^{-13}$	422.0		
$3.1 \times 10^{-13} \exp[-(270 \pm 220)/T]$	250-298	Tully et al., 1981	FP-RF (d)
$(1.04 \pm 0.08) \times 10^{-12}$	250		
$(1.20 \pm 0.09) \times 10^{-12}$	270		
$(1.24 \pm 0.09) \times 10^{-12}$	298		
$(5.43 \pm 0.23) \times 10^{-13}$	542		
$(6.39 \pm 0.29) \times 10^{-13}$	621		
$(6.82 \pm 0.74) \times 10^{-13}$	630		
$(6.06 \pm 0.34) \times 10^{-13}$	653		
$(1.02 \pm 0.04) \times 10^{-12}$	715		
$(1.20 \pm 0.16) \times 10^{-12}$	742		
$(1.59 \pm 0.09) \times 10^{-12}$	817		
$(1.90 \pm 0.20) \times 10^{-12}$	895		
$(2.26 \pm 0.13) \times 10^{-12}$	917		
$(2.35 \pm 0.23) \times 10^{-12}$	981		
$(2.20 \pm 0.34) \times 10^{-12}$	1017		
$(7.6 \pm 1.5) \times 10^{-13}$	244	Lorenz and Zellner, 1983	PLP-RF (e)
$(1.15 \pm 0.25) \times 10^{-12}$	298 ± 2		
$(1.26 \pm 0.25) \times 10^{-12}$	336		
$(8.3 \pm 1.7) \times 10^{-13}$	373		
$(5.0 \pm 1.0) \times 10^{-13}$	384		
$(4.0 \pm 0.9) \times 10^{-13}$	453		
$(4.3 \pm 0.9) \times 10^{-13}$	523		
$(8.8 \pm 0.4) \times 10^{-13}$	295	Wahner and Zetzsch, 1983	FP-RF (f)
$(1.02 \pm 0.2) \times 10^{-12}$	296	Rinke and Zetzsch, 1984	FP-RF (f)
$3.5 \times 10^{-11} \exp[-(2300 \pm 100)/T]$	787-1409	Madronich and Felder, 1985	FP-RF
$2.3 \times 10^{-12} \exp[-(190 \pm 60)/T]$	239-354	Witte et al., 1986	FP-RF (g)
$(1.05 \pm 0.05) \times 10^{-12}$	299		
$(1.40 \pm 0.23) \times 10^{-12}$	234	Wallington et al., 1987	PF-RF (h)
$(1.30 \pm 0.19) \times 10^{-12}$	263		

$(1.29 \pm 0.14) \times 10^{-12}$	296		
$(1.93 \pm 0.37) \times 10^{-13}$	393		
$(2.58 \pm 0.34) \times 10^{-13}$	438		
$k_1 = (4.6 \pm 2.8) \times 10^{-14}$	298	Knispel et al., 1990	FP-RF (i)
$k_2 = (1.06 \pm 0.09) \times 10^{-12}$	298		
$k_1 = (1.9 \pm 1.2) \times 10^{-14}$	315		
$k_2 = (1.02 \pm 0.03) \times 10^{-12}$	315		
$k_1 = (1.2 \pm 0.6) \times 10^{-14}$	333		
$k_2 = (1.05 \pm 0.12) \times 10^{-12}$	333		
$k_1 = (2.1 \pm 0.9) \times 10^{-14}$	354		
$k_2 = (8.8 \pm 2.3) \times 10^{-13}$	354		
$2.0 \times 10^{-14} \exp[(1420 \pm 250)/T]$	345-385	Lin et al., 1994	PLP-LIF (j)
$(1.09 \pm 0.04) \times 10^{-12}$	345-361		
$(1.2 \pm 0.2) \times 10^{-12}$	298	Bjergbakke et al., 1996	PR-UVA (k)
$(1.10 \pm 0.07) \times 10^{-12}$	297 ± 2	Bohn and Zetzsch, 1999	PLP-UVA (l)
$(1.06 \pm 0.07) \times 10^{-12}$	297 ± 2		
$8.0 \text{ x } 10^{-11} \exp[-(3199 \pm 241)/T]$	908-1736	Seta et al., 2006	SH-LIF (m)
Relative Rate Cofficients			
$\leq 2.4 \times 10^{-12}$	304 ± 1	Doyle et al., 1975	RR (n)
7.7×10^{-13}	300	Cox et al., 1980	RR (o)
8.6×10^{-13}	300	Barnes et al., 1982	RR (p)
$(1.35 \pm 0.06) \times 10^{-12}$	~298	Ohta and Ohyama, 1985	RR (q)
$(1.19 \pm 0.44) \times 10^{-12}$	296 ± 1	Edney et al., 1986	RR (r)
$(1.19 \pm 0.47) \times 10^{-12}$	297 ± 2	Sommerlade et al., 1993	RR (s)
$2.93 \times 10^{-12} \exp[-(288.3 \pm 84.8)/T]$	274-363	Semadeni et al., 1995	RR (t)
$(1.12 \pm 0.06) \times 10^{-12}$	299		
$(0.92 \pm 0.01) \times 10^{-12}$	248	Han et al., 2018	RR (u)
$(1.08 \pm 0.02) \times 10^{-12}$	288		

Comments

(a) At 100 Torr (133 mbar) of He diluent. Lower rate coefficients were measured at 3 and 20 Torr (4 and 27 mbar) of He diluent.

(b) Measured rate coefficient was independent of the pressure of Ar diluent over the range 50-600 Torr (67-800 mbar).

(c) Biexponential HO radical decays were observed at temperatures between 331 K and 381 K. Rate coefficients were measured at 100 Torr (133 mbar) of Ar diluent.

(d) Experiments were generally carried out at 100 Torr (133 mbar) pressure of Ar diluent. At 298 K, the rate coefficient was measured as a function of total pressure over the ranges 25-100 Torr (33-133 mbar) of He, 50-200 Torr (67-267 mbar) of Ar, and at 100 Torr (133 mbar) of SF_6, with no significant pressure dependence being observed over these ranges. Non-exponential HO radical decays were observed at temperatures between 320 K and 400 K.

(e) At 298 ± 2 K, rate coefficients were measured over the pressure range 1.5-112 mbar (1.1-84 Torr) of Ar diluent. The rate coefficients increased with increasing pressure up to ~40 mbar (30 Torr), with no observed effect of pressure above 40 mbar.

(f) Rate coefficients were measured over the pressure ranges 67-173 mbar (50-130 Torr) of Ar diluent (Wahner and Zetzsch, 1983) and 33-666 mbar (25-500 Torr) of He diluent (Rinke and Zetzsch, 1984), with a slight decrease in rate coefficient being observed below 133 mbar (100 Torr) pressure in both cases. The cited rate coefficients are at 133 mbar pressure.

(g) Rate coefficients were measured at 133 and/or 200 mbar pressure of Ar diluent (the 299 K rate coefficient cited in the table is at 133 mbar pressure). At 294 K, rate coefficients were also measured over the pressure range 1.3-533 mbar (1.0-400 Torr) of Ar diluent, with a decrease in rate coefficient being observed below ~67 mbar (50 Torr) pressure.

(h) No effect of pressure was observed over the range 25-50 Torr (33-67 mbar) of Ar diluent. Biexponential HO radical decays were observed at 353 K.

(i) Rate coefficients k_1 and k_2 were derived from fitting the observed non-exponential HO radical decays, measured over time periods at a total pressure of 133 mbar of Ar, to reactions (1), (2), the back-decomposition of the HO-benzene adduct and accounting for diffusive and background losses of HO radicals and the HO-benzene adduct. Using the rate coefficients of Tully et al. (1981) at 500-1000 K and the expression $k_1 = C\,T^2 \exp(-D/T)$, a global fit to the experimental data resulted in rate coefficients k_1 of 6.6×10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K, 1.0×10^{-14} cm^3 molecule^{-1} s^{-1} at 315 K, 1.5×10^{-14} cm^3 molecule^{-1} s^{-1} at 333 K and 2.2×10^{-14} cm^3 molecule^{-1} s^{-1} at 354 K.

(j) Rate coefficients k were derived from fitting the observed non-exponential HO radical decays, measured over time periods at total pressures of 250-500 Torr (333-667 mbar) of He, to reactions (1), (2), the back-decomposition of the HO-benzene adduct and accounting for diffusive and background losses of HO radicals and the HO-benzene adduct. The cited Arrhenius expression over the temperature range 345-385 K was obtained assuming that $k_1 = 0$.

(k) *k* was determined from the decay rates of HO radicals monitored by absorption at 309 nm.

(l) Experiments were carried out in N_2 and O_2 diluent at total pressures of 0.101-1.00 bar (75-750 Torr) of N_2 and 0.973-0.980 bar (730-735 Torr) of O_2, with measured rate coefficients of $(1.10 \pm 0.07) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in N_2 and $(1.06 \pm 0.07) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in O_2.

(m) HO radicals were generated by shock heating of nitric acid or *tert*-butyl hydroperoxide.

(n) HO radicals generated by the photolysis of organic-NO_x mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of benzene and *n*-butane (the reference compound) by GC. The measured rate coefficient ratio *k(*HO + benzene)/*k*(HO + *n*-butane) ≤ 1 is placed on an absolute basis using a rate coefficient of *k*(HO + *n*-butane) = 2.41×10^{-12} cm^3 molecule^{-1} s^{-1} at 304 K (IUPAC, 2019).

(o) HO radicals generated by the photolysis of HONO at 300-450 nm in air at atmospheric pressure. Benzene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + benzene)/*k*(HO + ethene) is placed on an absolute basis using a rate coefficient of *k*(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air (IUPAC, 2019).

(p) HO radicals were generated by dark decomposition of $HOONO_2$ in the presence of NO at atmospheric pressure of N_2 or air. Benzene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + benzene)/*k*(HO + ethene) = 0.11 is placed on an absolute basis using a rate coefficient of *k*(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air (IUPAC, 2019).

(q) HO radicals generated by the photolysis of H_2O_2 at 254 nm at atmospheric pressure. Experiments were carried out at room temperature (the specific temperature not being noted). Benzene and *n*-hexane (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + benzene)/*k*(HO + *n*-hexane) = 0.26 ± 0.01 is placed on an absolute basis using a 298 K rate coefficient of *k*(HO + *n*-hexane) = 5.20×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(r) HO radicals generated by the photolysis of CH_3ONO in air at 1 bar pressure. Benzene and propane (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + benzene)/*k*(HO + propane) is placed on an absolute basis using a rate coefficient of k(HO + propane) = 1.08×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, 2019).

(s) HO radicals generated by the photolysis of NO$_x$ in the presence of organics in air at 70 Torr (93 mbar) pressure. Benzene and *n*-hexane (the reference compound) were monitored by MS, and the measured rate coefficient ratio k(HO + benzene)/k(HO + *n*-hexane) is placed on an absolute basis using a rate coefficient of k(HO + *n*-hexane) = 5.17×10^{-12} cm^3 molecule^{-1} s^{-1} at 297 K (Atkinson and Arey, 2003).

(t) HO radicals generated by the photolysis of CH$_3$ONO in air at atmospheric pressure. Benzene and toluene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + benzene)/k(HO + toluene) = 1.625 exp[-(628.3 ± 84.8)/T] over the temperature range 274-363 K is placed on an absolute basis using a rate coefficient of k(HO + toluene) = 1.8×10^{-12} exp(340/T) cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(u) The rate coefficient was measured at atmospheric pressure of purified air in a photochemical reactor (3.2 m^3 glass chamber) by the relative rate technique. HO radicals were generated by the photolysis of CH$_3$ONO at wavelengths > 300 nm. The concentrations of benzene and the reference compounds (toluene and *n*-pentane) were measured by GC-FID. The measured rate coefficient ratios of k(HO + benzene)/k(HO + toluene) and k(HO + benzene)/k(HO + *n*-pentane) were not given by the authors, they were placed on an absolute basis using k(HO + toluene) = 7.09×10^{-12} at 248 K and 5.86×10^{-12} at 288 K and k(HO + *n*-pentane) = 2.93×10^{-12} at 248 K 3.62×10^{-12} at 288 K HO + toluene The values in the table are the average of the data obtained relative to HO + toluene and HO + *n*-pentane.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.2×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	2.3×10^{-12} exp(-190/T)	230-350
k_1 /cm^3 molecule^{-1} s^{-1}	8×10^{-15}	298
k_1 /cm^3 molecule^{-1} s^{-1}	3.8×10^{-11} exp(-2520/T)	330-1410
Reliability		
$\Delta \log k$	± 0.06	298
Δ E/R	± 200	230-350
$\Delta \log k_1$	± 0.5	298
Δ E$_1$/R	± 300	330-1410

Comments on Preferred Values

Absolute rate studies show that the reaction of HO radicals with benzene can be considered as comprising three temperature regimes (Perry et al., 1977; Tully et al., 1981). At temperatures <325-350 K the reaction proceeds by channels (1) and (2), with pathway (2) dominating and with the HO-benzene adduct, HOC$_6$H$_6$, being thermally stable against back-decomposition to reactants at total pressures above ~100 Torr. At total pressures <50-100 Torr, channel (2) is in the falloff regime at room temperature (Davis et al., 1975; Lorenz and Zellner, 1983; Wahner and Zetzsch, 1983; Rinke and Zetzsch, 1984; Witte and Zetzsch, 1986; Baulch et al., 1988; Goumri et al., 1991), with a limiting low-pressure rate coefficient at 297 ± 3 K of k_0(He) = 1.7×10^{-29} cm^6 molecule^{-2} s^{-1} (Goumri et al., 1991). At temperatures >450 K, decomposition of the

HO-benzene adduct back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1). At temperatures in the range ~325-450 K, decomposition of the HO-benzene adduct is significant and the measured rate coefficients depend on the experimental conditions, and in absolute rate studies biexponential HO radical decays are generally observed.

The >450 K rate coefficients of Tully et al. (1981), Lorenz and Zellner (1983) and Madronich and Felder (1985), which are attributed to those for pathway (1), and the values of k_1 derived by Knispel et al. (1990) from HO radical decay curves at 298-354 K indicate that an Arrhenius fit is adequate. The preferred values of k_1 are obtained from a least-squares fit of the >450 K rate coefficients of Tully et al. (1981), Lorenz and Zellner (1983) and Madronich and Felder (1985) and the rate coefficients k_1 of Knispel et al. (1990) at 333 K and 354 K (their rate coefficients k_1 at 298 K and 315 K have high associated uncertainties and are significantly higher than the rate coefficients k_1 derived by Knispel et al. (1990) from a global fit (see Comment (i)), and are therefore not used in the evaluation of k_1). The shock tube data of Seta et al. (2006) at 908-1736 K are in excellent agreement with this preferred expression for k_1.

The preferred values of k at ≤350 K are based on the absolute rate coefficients of Hansen et al. (1975), Perry et al. (1977), Tully et al. (1981), Lorenz and Zellner (1983), Witte et al. (1985) [which are judged to supersede the earlier room temperature studies of Wahner and Zetzsch (1983) and Rinke and Zetzsch (1984)], Wallington et al. (1987), Knispel et al. (1990) and Bohn and Zetzsch (1999). The rate coefficients at ≤350 K of Cox et al. (1981), Barnes et al. (1982), Wahner and Zetzsch (1983), Rinke and Zetzsch (1984), Ohta and Ohyama et al. (1985), Edney et al. (1986), Sommerlade et al. (1993), Lin et al. (1994), Semadeni et al. (1995) and Bjergbakke et al. (1996) are in good agreement with the preferred ≤350 K rate expression. While the rate coefficients derived by Lin et al. (1994) from non-exponential HO radical decays over the restricted temperature range 345-385 K show a negative temperature dependence, this arises from the rate coefficients at ≥367 K and may be due to fall-off effects; their rate coefficients at 345-361 K are independent of temperature and ~20% lower than the preferred values. Particularly noteworthy is that the rate coefficients of Semadeni et al. (1995) measured relative to those for toluene are in excellent agreement with the preferred expression, indicating that the preferred values for HO + benzene and HO + toluene (IUPAC, 2019) are internally self-consistent.

At atmospherically-relevant temperatures, the reaction proceeds essentially totally by channel (2), with channel (1) accounting for <2% of the overall reaction at 298 K and even less at lower temperatures.

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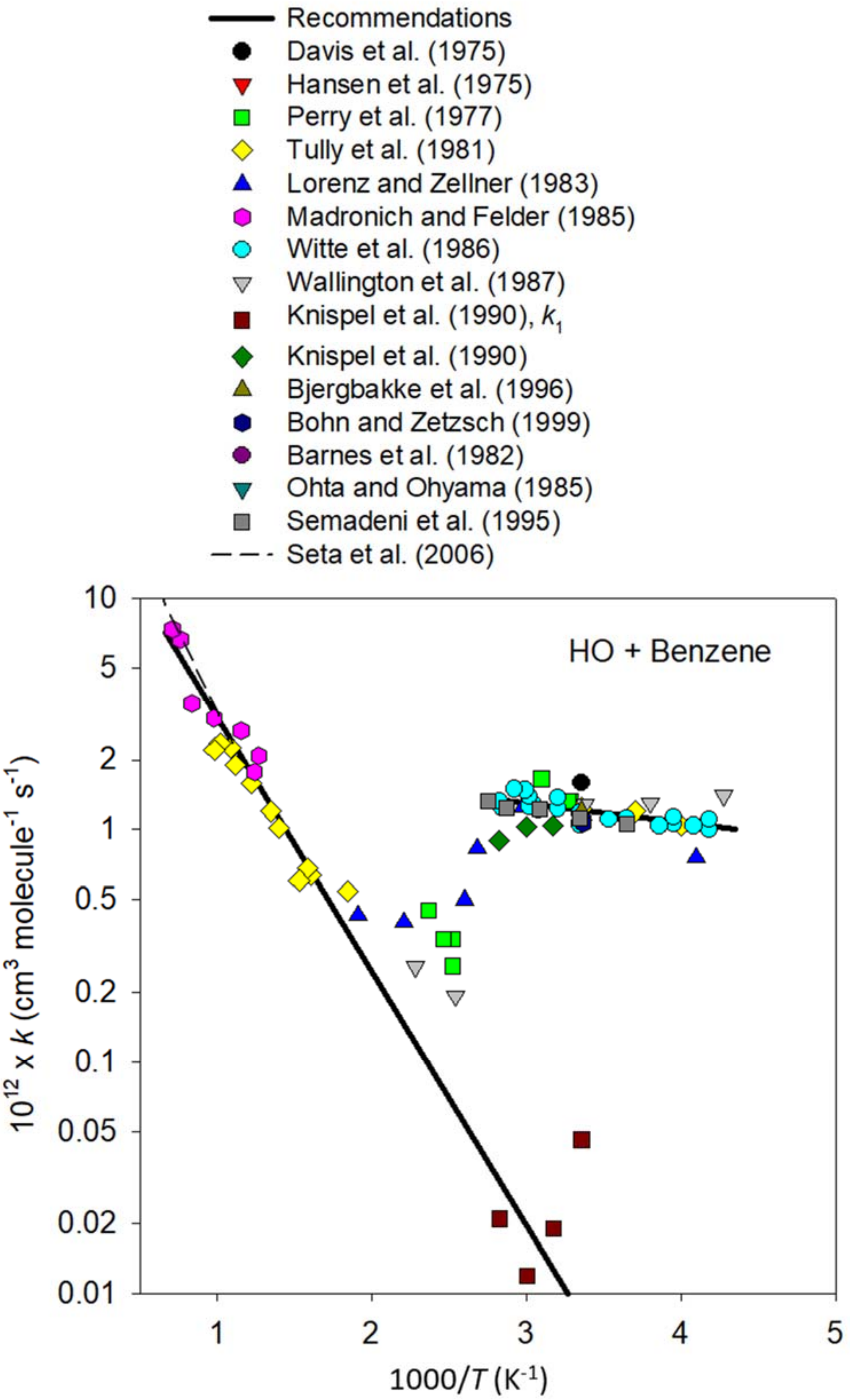
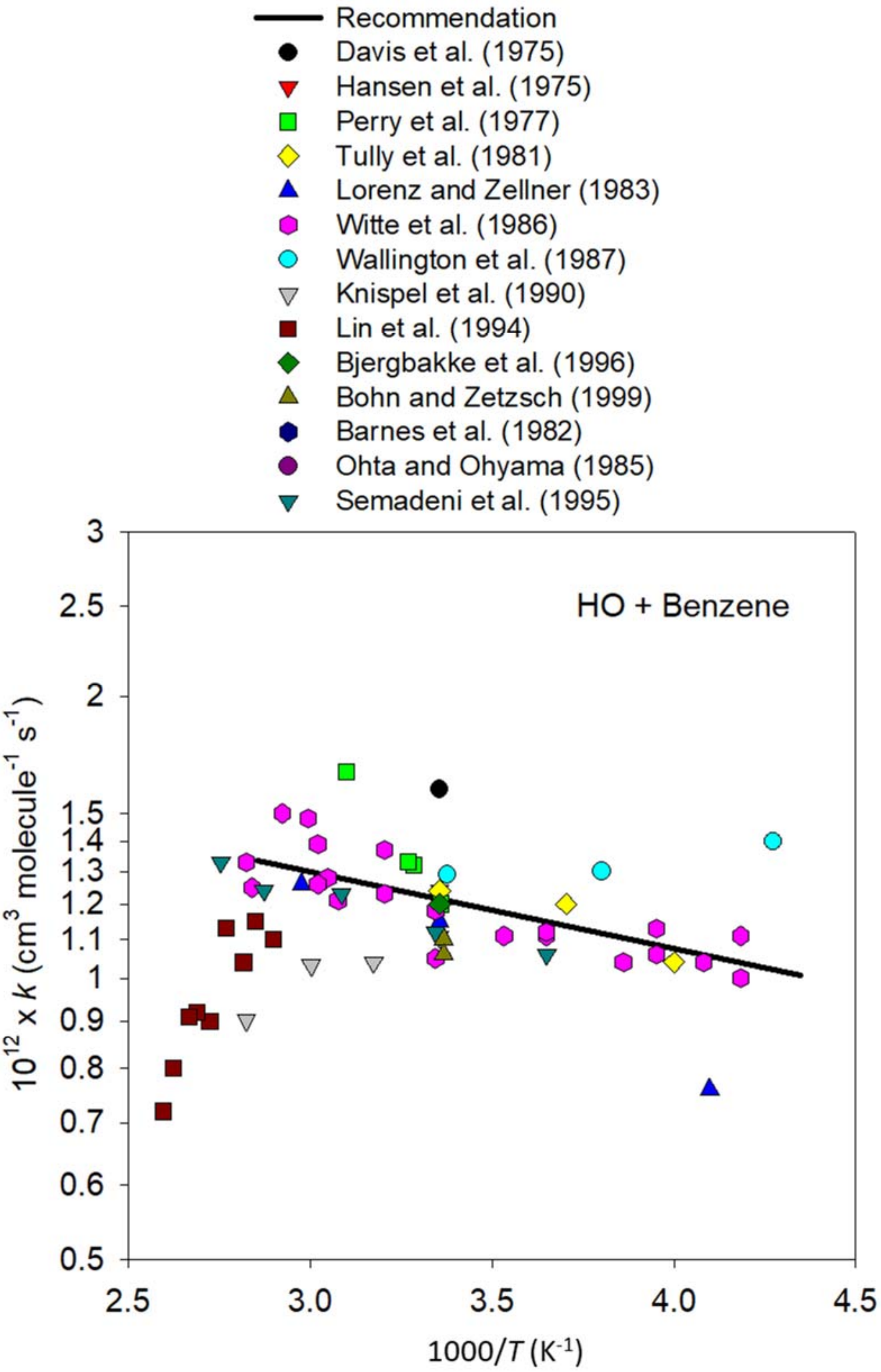


Rate coefficients for HO + Benzene.



Rate coefficients for HO + benzene.

HOx_AROM2: toluene

Last evaluated: September 2008; Last change in preferred values: September 2008

$$\mathrm{HO} + \mathrm{C_6H_5CH_3} \rightarrow \mathrm{H_2O} + \mathrm{C_6H_5CH_2} \quad (1)$$
$$\rightarrow \mathrm{HOC_6H_5CH_3} \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(6.11 \pm 0.40) \times 10^{-12}$	298	Davis et al., 1975	FP-RF (a)
$(5.78 \pm 0.58) \times 10^{-12}$	298	Hansen et al., 1975	FP-RF (b)
$(6.40 \pm 0.64) \times 10^{-12}$	297.9	Perry et al., 1977	FP-RF (c)
$(4.90 \pm 0.6) \times 10^{-12}$	323.7		
$(1.49 \pm 0.22) \times 10^{-12}$	379.2		
$(1.58 \pm 0.24) \times 10^{-12}$	394.2		
$(1.69 \pm 0.25) \times 10^{-12}$	408.7		
$(1.76 \pm 0.18) \times 10^{-12}$	424.4		
$(1.71 \pm 0.20) \times 10^{-12}$	472.7		
$3.8 \times 10^{-12} \exp[(180 \pm 170)/T]$	213-298	Tully et al., 1981	FP-RF (d)
$(8.20 \pm 0.54) \times 10^{-12}$	213		
$(8.73 \pm 0.39) \times 10^{-12}$	231		
$(7.97 \pm 0.56) \times 10^{-12}$	250		
$(8.53 \pm 0.37) \times 10^{-12}$	260		
$(7.44 \pm 0.55) \times 10^{-12}$	270		
$(6.36 \pm 0.69) \times 10^{-12}$	298		
$(2.16 \pm 0.08) \times 10^{-12}$	504		
$(2.45 \pm 0.05) \times 10^{-12}$	568		
$(2.49 \pm 0.12) \times 10^{-12}$	568		
$(3.26 \pm 0.29) \times 10^{-12}$	666		
$(3.58 \pm 0.16) \times 10^{-12}$	694		
$(4.67 \pm 0.19) \times 10^{-12}$	793		
$(5.54 \pm 0.27) \times 10^{-12}$	868		
$(6.87 \pm 0.23) \times 10^{-12}$	958		
$(9.5 \pm 1.0) \times 10^{-12}$	1046		
$k_1 = (0 \pm 2.0) \times 10^{-13}$	299	Knispel et al., 1990	FP-RF (e)
$k_2 = (7.0 \pm 2.1) \times 10^{-12}$	299		
$k_1 = (4.5 \pm 2.1) \times 10^{-13}$	311		
$k_2 = (5.6 \pm 0.4) \times 10^{-12}$	311		
$k_1 = (5.0 \pm 0.6) \times 10^{-13}$	323		
$k_2 = (5.0 \pm 0.3) \times 10^{-12}$	323		
$k_1 = (6.2 \pm 0.9) \times 10^{-13}$	340		
$k_2 = (3.8 \pm 0.9) \times 10^{-12}$	340		
$(6.4 \pm 0.7) \times 10^{-12}$	338	Markert and Pagsberg, 1993	PR-UVA (f)
$(5.60 \pm 0.14) \times 10^{-12}$	299 ± 2	Bohn, 2001	PLP-UVA (g)
$(5.70 \pm 0.19) \times 10^{-12}$	299 ± 2		
Relative Rate Cofficients			
$(3.4 \pm 1.5) \times 10^{-12}$	304 ± 1	Doyle et al., 1975	RR (h)
7.0×10^{-12}	300	Cox et al., 1980	RR (i)

$(5.62 \pm 0.16) \times 10^{-12}$	~298	Ohta and Ohyama, 1985	RR (j)
$(5.07 \pm 0.52) \times 10^{-12}$	297	Edney et al., 1986	RR (k)
$(5.93 \pm 0.16) \times 10^{-12}$	296 ± 2	Atkinson and Aschmann, 1989	RR (l)
$(6.35 \pm 1.50) \times 10^{-12}$	297 ± 2	Sommerlade et al., 1993	RR (m)
$(5.56 \pm 0.26) \times 10^{-12}$	298	Finlayson-Pitts et al., 1993	RR (n)
$2.09 \times 10^{-18} T^2 \exp[(207.4 \pm 113.5)/T]$	284-363	Semadeni et al., 1995	RR (o)
$(5.62 \pm 0.29) \times 10^{-12}$	299		
$(5.39 \pm 0.07) \times 10^{-12}$	276	Anderson and Hites, 1996	RR (p,q)
$(5.84 \pm 0.07) \times 10^{-12}$	285		
$(5.58 \pm 0.14) \times 10^{-12}$	285		
$(5.34 \pm 0.07) \times 10^{-12}$	293		
$(5.61 \pm 0.08) \times 10^{-12}$	303		
$(5.47 \pm 0.08) \times 10^{-12}$	310		
$(5.43 \pm 0.16) \times 10^{-12}$	323		
$(5.13 \pm 0.16) \times 10^{-12}$	323		
$(5.05 \pm 0.08) \times 10^{-12}$	323		
$(5.22 \pm 0.16) \times 10^{-12}$	324		
$(5.07 \pm 0.08) \times 10^{-12}$	324		
$(4.96 \pm 0.17) \times 10^{-12}$	344		
$(4.77 \pm 0.09) \times 10^{-12}$	363		
$(3.36 \pm 0.19) \times 10^{-12}$	371		
$(2.94 \pm 0.19) \times 10^{-12}$	383		
$(5.61 \pm 0.56) \times 10^{-12}$	296	Anderson and Hites, 1996	RR (p,r)
$(5.35 \pm 0.21) \times 10^{-12}$	297		
$(5.28 \pm 0.42) \times 10^{-12}$	297		
$(5.21 \pm 0.21) \times 10^{-12}$	297		
$(4.82 \pm 0.08) \times 10^{-12}$	323		
$(5.21 \pm 0.16) \times 10^{-12}$	323		
$(4.67 \pm 0.16) \times 10^{-12}$	323		
$(4.90 \pm 0.08) \times 10^{-12}$	323		
$(4.61 \pm 0.16) \times 10^{-12}$	324		
$(4.60 \pm 0.09) \times 10^{-12}$	363		
$(4.51 \pm 0.09) \times 10^{-12}$	363		
$(4.60 \pm 0.27) \times 10^{-12}$	363		
$(4.51 \pm 0.09) \times 10^{-12}$	363		
$(4.42 \pm 0.98) \times 10^{-12}$	363		
$(4.42 \pm 0.09) \times 10^{-12}$	363		
$(5.55 \pm 0.07) \times 10^{-12}$	296 ± 2	Kramp and Paulson, 1998	RR (s,t)
$(5.15 \pm 0.11) \times 10^{-12}$	296 ± 2	Kramp and Paulson, 1998	RR (s,t)
$(6.25 \pm 0.07) \times 10^{-12}$	296 ± 2	Kramp and Paulson, 1998	RR (s,u)
$(5.36 \pm 0.08) \times 10^{-12}$	296 ± 2	Kramp and Paulson, 1998	RR (s,v)
Branching Ratios			
$k_1/k = 0.728\ 0.082$	298 ± 2	Atkinson et al., 1989	(w)
$k_1/k_2 < 0.022$	299	Knispel et al., 1990	FP-RF (e)
$k_1/k_2 = 0.08 \pm 0.04$	311		
$k_1/k_2 = 0.10 \pm 0.02$	323		
$k_1/k_2 = 0.16 \pm 0.05$	340		
$k_1/k = 0.11 \pm 0.02$	338	Markert and Pagsberg, 1993	PR-UVA (x)
$k_1/k = 0.067 \pm 0.07$	298	Smith et al., 1998	(y)
$k_1/k = 0.065 \pm 0.09$	~298	Klotz et al., 1998	(z)
$(6.81 \pm 0.07) \times 10^{-12}$	248	Han et al., 2018	(zz)

$(5.69 \pm 0.06) \times 10^{-12}$	288

Comments

(a) At 100 Torr (133 mbar) of He diluent. Lower rate coefficients were measured at 3 and 20 Torr (4 and 27 mbar) of He diluent.

(b) Measured rate coefficient was independent of the pressure of Ar diluent over the range 100-619 Torr (133-825 mbar).

(c) Non-exponential HO radical decays were observed at temperatures between 325 K and 379 K. No effect of increasing the total pressure at 325 K, 378 K or 424 K from 100 Torr to 200 Torr (133-267 mbar) of argon diluent was observed on the measured rate coefficients (at 325 K and 378 K these were derived from the initial HO radical decay rates).

(d) Experiments were generally carried out at 100 Torr (133 mbar) pressure of Ar diluent. At 298 K, the rate coefficient was measured as a function of total pressure over the ranges 20-100 Torr (27-133 mbar) of He, 25-100 Torr (33-133 mbar) of Ar, and at 100 Torr (133 mbar) of SF_6, and the 298 K rate coefficient appeared to reach the high-pressure value at ~100 Torr pressure. Non-exponential HO radical decays were observed at temperatures between 320 K and 380 K.

(e) Rate coefficients k_1 and k_2 were derived from fitting the observed biexponential HO radical decays, measured over time periods at a total pressure of 133 mbar of Ar, to reactions (1), (2), the back-decomposition of the HO-toluene adduct and accounting for diffusive and background losses of HO radicals and the HO-toluene adduct. Using the rate coefficients of Tully et al. (1981) at 500-1000 K and the expression $k_1 = C\,T^2 \exp(-D/T)$, a global fit to the experimental data resulted in rate coefficients k_1 of 4.3×10^{-13} cm^3 molecule^{-1} s^{-1} at 299 K, 4.8×10^{-13} cm^3 molecule^{-1} s^{-1} at 311 K, 5.3×10^{-13} cm^3 molecule^{-1} s^{-1} at 323 K and 6.1×10^{-13} cm^3 molecule^{-1} s^{-1} at 340 K.

(f) k was determined from the formation kinetics of the HO-toluene adduct monitored by UV absorption at 300 nm.

(g) Experiments were carried out in N_2 and O_2 diluent at a total pressure of 750 Torr (1 bar), with rate coefficients of $(5.70 \pm 0.19) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in N_2 and $(5.60 \pm 0.14) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in O_2.

(h) HO radicals generated by the photolysis of organic-NO_x mixtures at atmospheric pressure in a 5870 L reaction chamber, with analyses of toluene and *n*-butane (the reference compound) by GC. The measured rate coefficient ratio k(HO + toluene)/k(HO + *n*-butane) = 1.4 ± 0.6 is placed on an absolute basis using a rate coefficient of k(HO + *n*-butane) = 2.41×10^{-12} cm^3 molecule^{-1} s^{-1} at 304 K (IUPAC, 2019).

(i) HO radicals generated by the photolysis of HONO at 300-450 nm in air at atmospheric pressure. Toluene and ethene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + ethene) is placed on an absolute basis using a rate coefficient of k(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} at 300 K and atmospheric pressure of air (IUPAC, 2019).

(j) HO radicals generated by the photolysis of H_2O_2 at 254 nm at atmospheric pressure. Experiments were carried out at room temperature (the specific temperature not being noted). Toluene and *n*-hexane (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + *n*-hexane) = 1.08 ± 0.03 is placed on an absolute basis using a 298 K rate coefficient of k(HO + *n*-hexane) = 5.20×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(k) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. Toluene and cyclohexane (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + cyclohexane) is placed on an absolute basis using a rate coefficient of k(HO + cyclohexane) = 6.95×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 297 K (Atkinson and Arey, 2003).

(l) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. Toluene and propene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + propene) = 0.206 ± 0.006 is placed on an absolute basis using k(HO + propene) = 2.88×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 296 K and atmospheric pressure of air (IUPAC, 2019).

(m) HO radicals generated by the photolysis of NO_x in the presence of organics in air at 70 Torr (93 mbar) pressure. Toluene and *n*-hexane (the reference compound) were monitored by MS, and the measured rate coefficient ratio k(HO + toluene)/k(HO + *n*-hexane) is placed on an absolute basis using k(HO + *n*-hexane) = 5.17×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 297 K (Atkinson and Arey, 2003).

(n) HO radicals were generated from the dark reactions of O_3 with toluene and *n*-hexane (the reference compound) in O_2 diluent at 14.1-19.4 Torr (19-26 mbar) pressure. Toluene and *n*-hexane were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + *n*-hexane) = 1.07 ± 0.05 is placed on an absolute basis using k(HO + *n*-hexane) = 5.20×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K (Atkinson and Arey, 2003).

(o) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. Toluene and 2,3-dimethylbutane (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + toluene)/k(HO + 2,3-dimethylbutane) = $0.126 \exp[(614.4 \pm 113.5)/T]$ over the temperature range 294-363 K is placed on an absolute basis using k(HO + 2,3-dimethylbutane) = $1.66 \times 10^{-17}\ T^2 \exp(407/T)$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003). Rate coefficients were also measured at 258 K, 264 K and 269 K but were not used by Semadeni et al. (1995) in their derivation of the Arrhenius expression.

(p) HO radicals generated by the photolysis of O_3 in the presence of water vapor at 254 nm in $N_2 + O_2$ or He diluent at atmospheric pressure. Toluene and cyclohexane (the reference compound) were monitored by MS, and the measured rate coefficient ratio k(HO + toluene)/k(HO + cyclohexane) are placed on an absolute basis using a rate coefficient of k(HO + cyclohexane) = $3.26 \times 10^{-17}\ T^2 \exp(262/T)$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(q) In He diluent.

(r) In $N_2 + O_2$ diluent.

(s) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. Toluene and 1,3-butadiene, propene or cyclohexane (the reference compounds) were monitored by GC, and the measured rate coefficient ratios k(HO + toluene)/k(HO + reference compound) are placed on an absolute basis using rate coefficients at 296 K and atmospheric pressure of air of k(HO + 1,3-butadiene) = 6.72×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003), k(HO + propene) = 2.88×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019) and k(HO + cyclohexane) = 6.92×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(t) Relative to 1,3-butadiene.

(u) Relative to propene.

(v) Relative to cyclohexane.

(w) Derived from the measured yields of benzaldehyde [C_6H_5CHO] plus benzyl nitrate [$C_6H_5CH_2ONO_2$] in irradiated CH_3ONO-NO-toluene-air mixtures at 298 ± 2 K and ~740 Torr of air. Benzaldehyde and benzyl nitrate are the first-generation products expected from reactions of benzyl radicals generated in channel (1).

(x) Pulse radiolysis study. Benzyl radicals were monitored at 253 nm and the derived benzyl radical concentration (calibrated using the Cl + toluene reaction to generate known concentrations of benzyl) were compared to the initial concentration of HO radicals generated in the reactions from the pulse radiolysis of Ar in the presence of H_2O.

(y) Derived from the measured yield of benzaldehyde [C_6H_5CHO] plus an estimated benzyl nitrate [$C_6H_5CH_2ONO_2$] yield in irradiated CH_3ONO-NO-toluene-air mixtures at 298 K and atmospheric pressure of air. Benzaldehyde and benzyl nitrate are the first-generation products expected from reactions of benzyl radicals generated in channel (1), and the benzyl nitrate yield is estimated using a yield ratio of benzyl nitrate/benzaldehyde = 0.12 (Hoshino et al., 1978; Atkinson et al., 1989).

(z) Derived from the measured yield of benzaldehyde [C_6H_5CHO] plus an estimated benzyl nitrate [$C_6H_5CH_2ONO_2$] yield in irradiated NO_x-toluene-air mixtures at ~298 K and atmospheric pressure of air. Benzaldehyde and benzyl nitrate are the first-generation products expected from reactions of benzyl radicals generated in channel (1), and the benzyl nitrate yield is estimated using a yield ratio of benzyl nitrate/benzaldehyde = 0.12 (Hoshino et al., 1978; Atkinson et al., 1989).

(v) (zz) The rate coefficient was measured at atmospheric pressure of purified air in a photochemical reactor (3.2 m^3 glass chamber) by the relative rate technique. HO radicals were generated by the photolysis of CH_3ONO at wavelengths > 300 nm. The concentrations of *n*-butane and *n*-pentane (the reference compounds) were measured by GC-FID. The measured rate coefficient ratios of k(HO + toluene)/k(HO + *n*-pentane) were not given by the authors, they were placed on an absolute basis k(HO + *n*-pentane) = 2.93×10^{-12} at 248 K 3.62×10^{-12} at 288 K (in cm^3 $molecule^{-1}$ s^{-1}). The values in the table are the average of the data obtained relative to HO + *n*-pentane from this work and the recommended values k(HO + toluene) from IUPAC (IUPAC, 2019).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	5.6×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	$1.8 \times 10^{-12} \exp(340/T)$	210-350
k_1 /cm^3 molecule^{-1} s^{-1}	3.5×10^{-13}	298
k_1 /cm^3 molecule^{-1} s^{-1}	$2.5 \times 10^{-11} \exp(-1270/T)$	310-1050
Reliability		
$\Delta \log k$	± 0.06	298
Δ E/R	± 200	210-350
$\Delta \log k_1$	± 0.20	298
$\Delta E_1/R$	± 200	310-1050

Comments on Preferred Values

Absolute rate studies show that the reaction of HO radicals with toluene can be considered as comprising three temperature regimes (Perry et al., 1977; Tully et al., 1981). At temperatures <325-350 K the reaction proceeds by channels (1) and (2), with pathway (2) dominating and with the HO-toluene adducts, $HOC_6H_5CH_3$, being thermally stable against back-decomposition to reactants at total pressures above ~100 Torr. At total pressures <100 Torr, channel (2) is in the falloff regime (Davis et al., 1975; Tully et al., 1981; Bourmada et al., 1988a,b), with a limiting low-pressure rate coefficient at 295 ± 2 K of k_o(He) = 4.0 x 10^{-28} cm^6 $molecule^{-2}$ s^{-1} (Bourmada et al., 1988a,b). At temperatures >450 K, decomposition of the HO-toluene adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1). At temperatures in the range ~325-450 K, decomposition of the HO-toluene adducts is significant and the measured rate coefficients depend on the experimental conditions, and in absolute rate studies biexponential HO radical decays are generally observed.

The >450 K rate coefficients of Perry et al. (1977) and Tully et al. (1981), which are attributed to those for pathway (1), and the values of k_1 derived by Knispel et al. (1990) from HO radical decay curves at 299-340 K indicate that an Arrhenius fit is adequate. The preferred values of k_1 are obtained from a least-squares fit of the >450 K rate coefficients of Perry et al. (1977) and Tully et al. (1981) and the rate coefficients k_1 of Knispel et al. (1990) at 323 K and 340 K (their rate coefficients k_1 at 299 K and 311 K have high associated uncertainties and are not used in the evaluation of k_1). The preferred values of k at ≤350 K are based on the absolute rate coefficients of Hansen et al. (1975), Perry et al. (1977), Tully et al. (1981), Knispel et al. (1990) [omitting the 299 K rate coefficient which has a high associated uncertainty] and Bohn (2001) and the relative rate studies of Edney et al. (1986), Atkinson and Aschmann (1989), Finlayson-Pitts et al. (1993), Semadeni et al. (1995), Anderson and Hites (1996) and Kramp and Paulson (1998). The rate coefficient ratio k_1/k derived from the preferred values (0.063 at 298 K) is in excellent agreement with the branching ratios obtained from product studies (Atkinson et al., 1989; Smith et al., 1998; Klotz et al., 1998).

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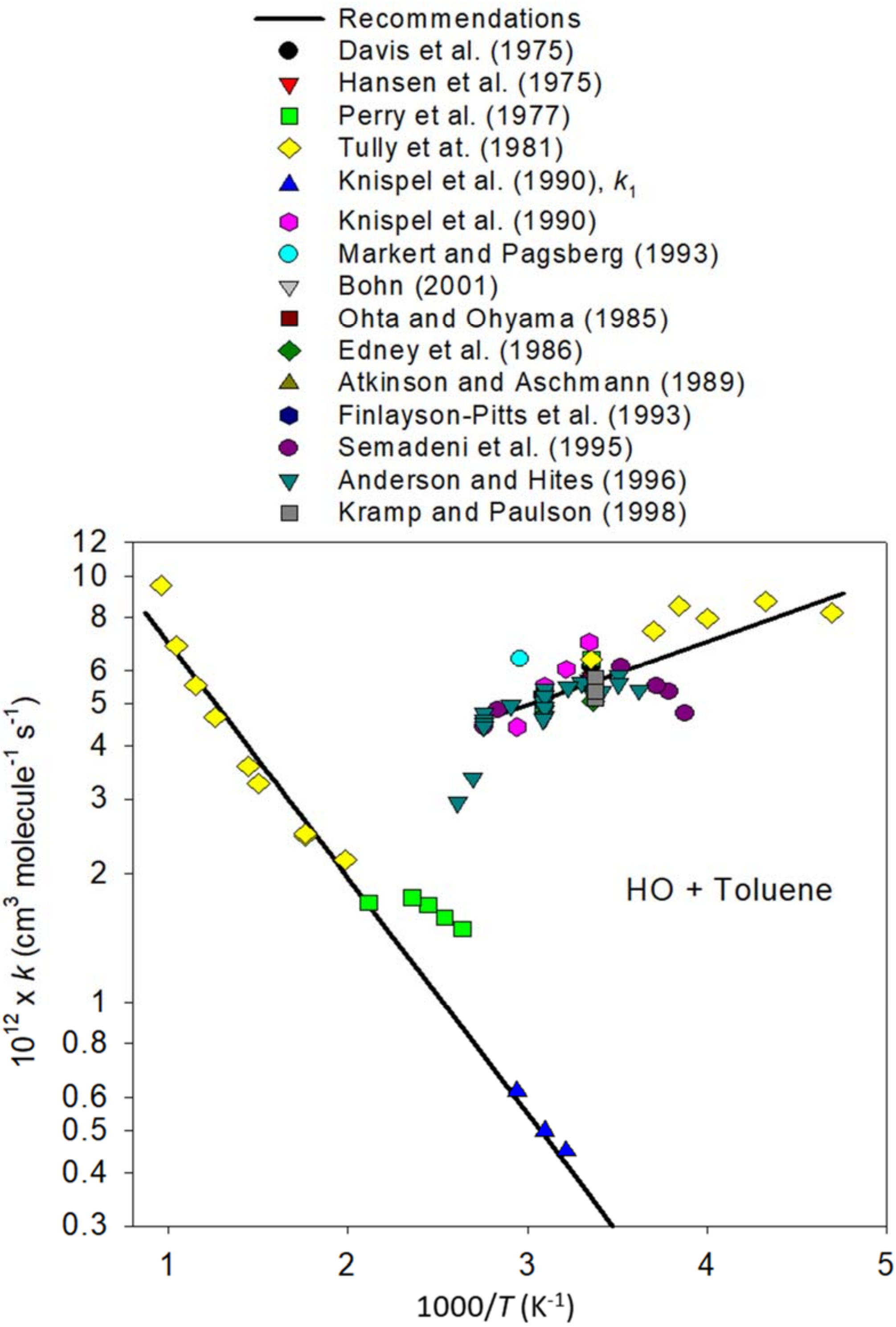
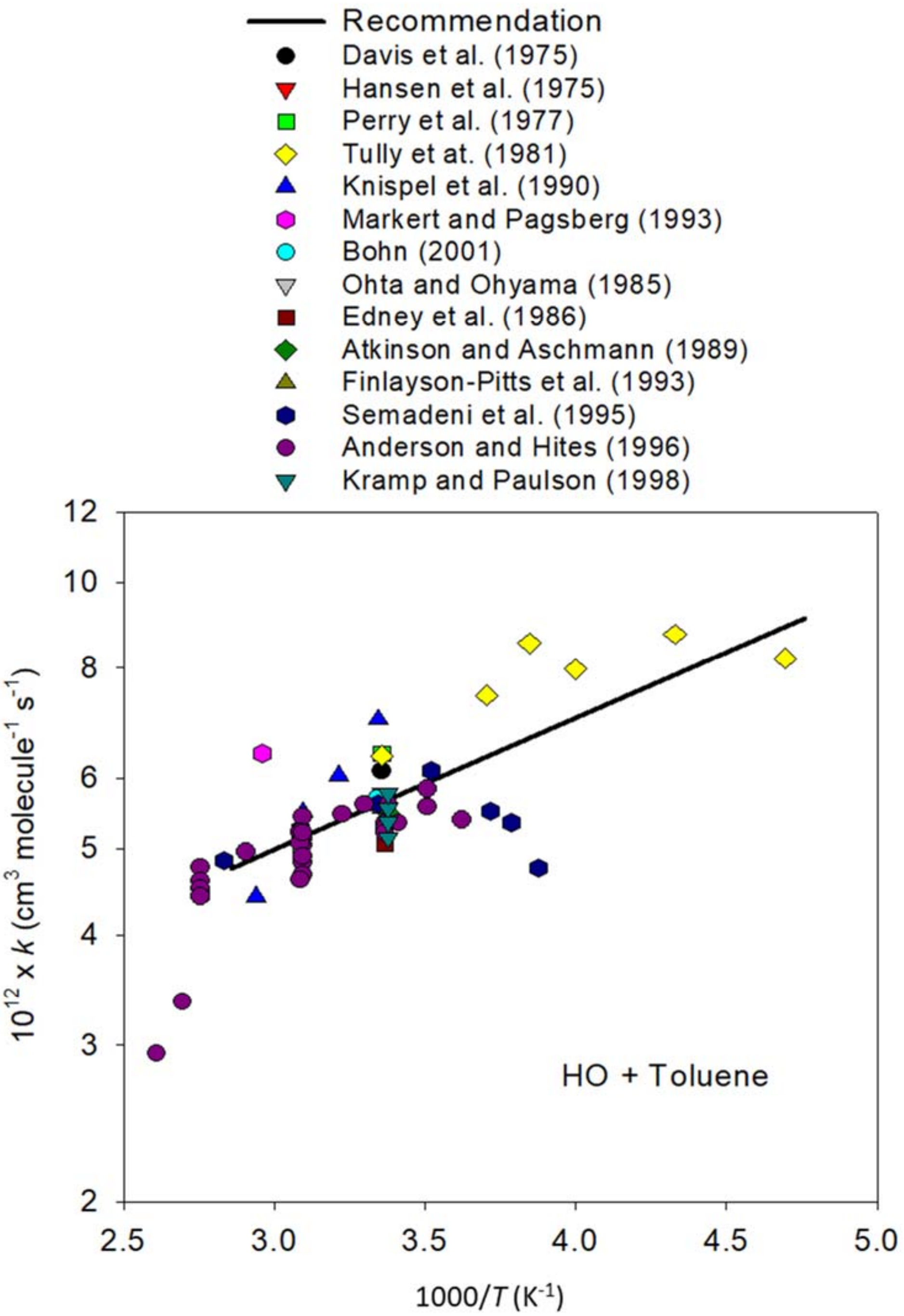


Rate coefficients for HO + toluene.



Rate coefficients for HO + toluene.

HOx_AROM3: *m*-cresol

Last evaluated: September 2008; Last change in preferred values: September 2008

HO + *m*-$CH_3C_6H_4OH$	**→ $H_2O + CH_3C_6H_4O$**	**(1)**
	→ $H_2O + CH_2C_6H_4OH$	**(2)**
	→ $CH_3C_6H_4(OH)_2$	**(3)**

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(5.77 \pm 0.33) \times 10^{-11}$	300 ± 1	Atkinson et al., 1978	RR (a)
$(7.34 \pm 0.43) \times 10^{-11}$	296 ± 2	Atkinson and Aschmann, 1990	RR (b)
$3.97 \times 10^{-12} \exp[(775.4 \pm 230.9)/T]$	299-373	Semadeni et al., 1995	RR (c)
$(5.42 \pm 0.54) \times 10^{-11}$	299		
$(5.78 \pm 0.91) \times 10^{-11}$	294 ± 2	Coeur-Tourneur et al., 2006	RR (d)

Comments

(a) HO radicals were generated by the photolysis of NO_x-organic-air mixtures in a ~5500 L Teflon chamber at wavelengths >300 nm at atmospheric pressure. The concentrations of *m*-cresol and *o*-cresol (the reference organics) were measured by GC. The measured rate coefficient ratio k(HO + *m*-cresol)/k(HO + *o*-cresol) = 1.42 ± 0.08 is placed on an absolute basis using a rate coefficient at 300 K of k(HO + *o*-cresol) = 4.06×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(b) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. The concentrations of *m*-cresol and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + *m*-cresol)/k(HO + propene) = 2.55 ± 0.15 is placed on an absolute basis using k(HO + propene) = 2.88×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K and atmospheric pressure of air (IUPAC, 2019).

(c) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Teflon chamber. *m*-Cresol and *o*-cresol (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + *m*-cresol)/k(HO + *o*-cresol) = $2.482 \exp[-(194.6 \pm 230.9)/T]$ over the temperature range 299-373 K is placed on an absolute basis using k(HO + *o*-cresol) = $1.6 \times 10^{-12} \exp(970/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(d) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~8000 L Plexiglas chamber. *m*-Cresol and 1,3,5-trimethylbenzene (the reference compound) were monitored by GC, and the measured rate coefficient ratios k(HO + *m*-cresol)/k(HO + 1,3,5-trimethylbenzene) = 1.02 ± 0.16 is placed on an absolute basis using k(HO + 1,3,5-trimethylbenzene) = 5.67×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	6.2×10^{-11}	298
k /cm^3 molecule^{-1} s^{-1}	$2.4 \times 10^{-12} \exp(965/T)$	290-350
Reliability		
$\Delta \log k$	± 0.10	298
Δ E/R	± 600	290-350

Comments on Preferred Values

As for the reactions of HO radicals with benzene, toluene, phenol and *o*-cresol (IUPAC, 2019), the reaction of HO radicals with *m*-cresol can be considered as comprising three temperature regimes. At temperatures <325-350 K the reaction proceeds by channels (1-3), with pathway (3) dominating and with the HO-cresol adducts being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (based on the analogous HO + phenol reaction (IUPAC, 2019)). At temperatures >400-450 K, decomposition of the HO-cresol adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1) and (2). At temperatures in the range ~325-400 K, decomposition of the HO-cresol adducts is significant and the measured rate coefficients depend on the experimental conditions.

The available rate coefficients (Atkinson et al., 1978; Atkinson and Aschmann, 1990; Semadeni et al., 1995; Coeur-Tourneur et al., 2006) are all from relative rate studies, with only one study being carried out as a function of temperature (Semadeni et al., 1995). At room temperature, the relative rate data of Atkinson et al. (1978), Atkinson and Aschmann (1990), Semadeni et al. (1995) and Coeur-Tourneur et al. (2006) are in reasonable agreement. The preferred temperature dependence is obtained from a least-squares analysis of the rate coefficients of Semadeni et al. (1995) at temperatures <350 K. The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Atkinson and Aschmann (1990) [which is judged to supersede the earlier study of Atkinson et al. (1978)], Semadeni et al. (1995) and Coeur-Tourneur et al. (2006), using the preferred temperature dependence to correct the measured rate coefficients to 298 K. The pre-exponential factor is adjusted to fit the 298 K preferred value. Note that no rate coefficients have been measured below 294 K. Furthermore, the rate coefficients used to derive the preferred temperature dependence may have been influenced by thermal decomposition of the HO-cresol adducts, and hence the preferred rate expression should not be used below ~290 K

By analogy with the HO + *o*-cresol reaction (Perry et al., 1977; IUPAC, 2019), at atmospherically-relevant temperatures the HO + *m*-cresol reaction is expected to proceed almost entirely by channels (1) and (3), with channel (1) accounting for a minor fraction (~4%) of the overall reaction at 298 K and for less at lower temperatures. In the presence of NO_x, Atkinson et al. (1992), Olariu et al. (2002) and Coeur-Tourneur et al. (2006) measured 5-methyl-2-nitrophenol plus 3-methyl-2-nitrophenol formation yields from the HO radical-initiated reaction of *m*-cresol to be 3.2 ± 1.5% at 296 ± 2 K, 7.7 ± 2.2% at 298 ± 2 K, and 2.9 ± 0.5% at 294 ± 2 K, respectively. Since 3- and 5-methyl-2-nitrophenol formation is attributed to the reaction of 3-methylphenoxy radicals with NO_2, these observations indicate that at room temperature channel (1) accounts for least 3% of the overall reaction, consistent with the kinetic data.

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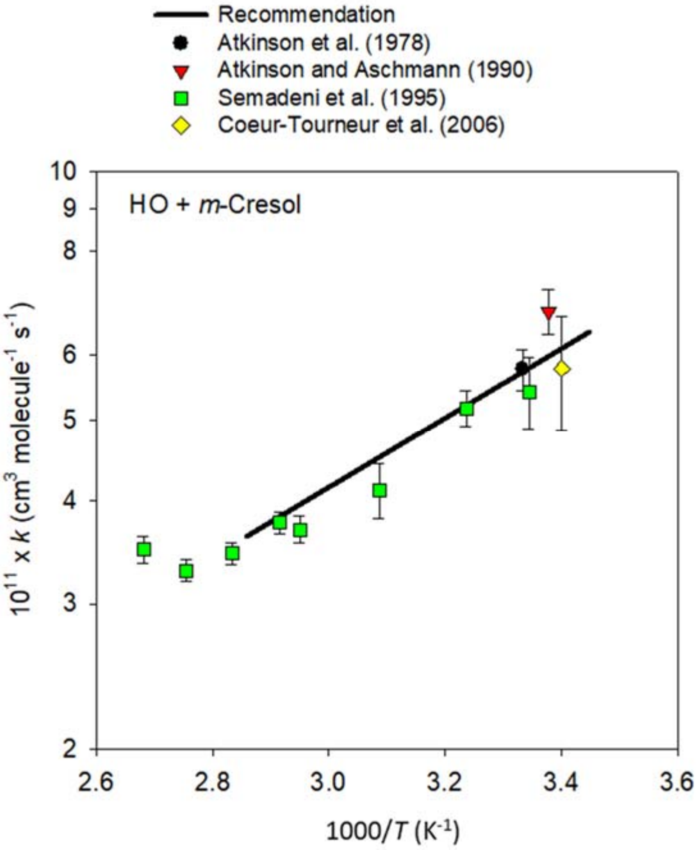

Rate coefficients for HO + *m*-cresol.

HOx_AROM4: *o*-cresol

Last evaluated: September 2008; Last change in preferred values: September 2008

$$\mathbf{HO + \textit{o}\text{-}CH_3C_6H_4OH \rightarrow H_2O + CH_3C_6H_4O \quad (1)}$$

$$\mathbf{\rightarrow H_2O + CH_2C_6H_4OH \quad (2)}$$

$$\mathbf{\rightarrow CH_3C_6H_4(OH)_2 \quad (3)}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.6 \times 10^{-12} \exp[(906 \pm 1007)/T]$	299-335	Perry et al., 1977	FP-RF (a)
$(3.41 \pm 0.68) \times 10^{-11}$	299.4		
$(2.93 \pm 0.59) \times 10^{-11}$	310.6		
$(2.98 \pm 0.60) \times 10^{-11}$	322.0		
$(2.68 \pm 0.54) \times 10^{-11}$	330.7		
$(2.55 \pm 0.51) \times 10^{-11}$	335.4		
$5.0 \times 10^{-11} \exp[-(906 \pm 1007)/T]$	400-424		
$(5.6 \pm 1.1) \times 10^{-12}$	400.6		
$(5.4 \pm 1.1) \times 10^{-12}$	407.8		
$(6.2 \pm 1.2) \times 10^{-12}$	423.1		
Relative Rate Cofficients			
$(3.85 \pm 0.33) \times 10^{-11}$	300 ± 1	Atkinson et al., 1978	RR (b)
$(4.61 \pm 0.22) \times 10^{-11}$	296 ± 2	Atkinson and Aschmann, 1990	RR (c)
$1.01 \times 10^{-12} \exp[(1155.6 \pm 246.1)/T]$	301-373	Semadeni et al., 1995	RR (d)
$(4.65 \pm 0.40) \times 10^{-11}$	301		
$(4.25 \pm 0.52) \times 10^{-11}$	294 ± 2	Coeur-Tourneur et al., 2006	RR (e)

Comments

(a) Non-exponential HO radical decays were observed at temperatures between 344 K and 393 K. The total pressure was ~100 Torr (133 mbar) of argon diluent.

(b) HO radicals were generated by the photolysis of NO_x-organic-air mixtures in a ~5500 L Teflon chamber at wavelengths >300 nm at atmospheric pressure. The concentrations of *o*-cresol and *n*-butane and 2,2-dimethylpropane (the reference organics) were measured by GC. The measured rate coefficient ratio k(HO + *o*-cresol)/{k(HO + *n*-butane) - k(HO + 2,2-dimethylpropane)} is placed on an absolute basis using rate coefficients at 300 K of k(HO + *n*-butane) = 2.38×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019) and k(HO + 2,2,-dimethylpropane)} = 8.4×10^{-13} cm^3 molecule^{-1} s^{-1} (Arey and Atkinson, 2003).

(c) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. The concentrations of *o*-cresol and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + *o*-cresol)/k(HO + propene) = 1.60 ± 0.08 is placed on an absolute basis using k(HO + propene) = 2.88×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K and atmospheric pressure of air (IUPAC, 2019).

(d) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Teflon chamber. *o*-Cresol and 1,3-butadiene (the reference compound) were monitored by GC, and the measured rate coefficient ratio *k*(HO + *o*-cresol)/*k*(HO + 1,3-butadiene) = 0.068 exp[(707.6 ± 246.1)/*T*] over the temperature range 301-373 K is placed on an absolute basis using *k*(HO + 1,3-butadiene) = 1.48 × 10^{-11} exp(448/*T*) cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(e) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~8000 L Plexiglas chamber. *o*-Cresol and 1,3,5-trimethylbenzene (the reference compound) were monitored by GC, and the measured rate coefficient ratios *k*(HO + *o*-cresol)/*k*(HO + 1,3,5-trimethylbenzene) = 0.75 ± 0.09 is placed on an absolute basis using *k*(HO + 1,3,5-trimethylbenzene) = 5.67 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 $molecule^{-1}$ s^{-1}	4.2 × 10^{-11}	298
k /cm^3 $molecule^{-1}$ s^{-1}	1.6 × 10^{-12} exp(970/*T*)	290-350
Relability		
Δ log *k*	± 0.10	298
Δ E/R	± 600	290-350

Comments on Preferred Values

As for the reactions of HO radicals with benzene and toluene (IUPAC, 2019), the reaction of HO radicals with *o*-cresol can be considered as comprising three temperature regimes (Perry et al., 1977). At temperatures <325-350 K the reaction proceeds by channels (1-3), with pathway (3) dominating and with the HO-cresol adducts being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (based on the analogous HO + phenol reaction (IUPAC, 2019)). At temperatures >400-450 K, decomposition of the HO-cresol adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1) and (2). At temperatures in the range ~325-400 K, decomposition of the HO-cresol adducts is significant and the measured rate coefficients depend on the experimental conditions, and in absolute rate studies non-exponential HO radical decays are observed (Perry et al., 1977).

At room temperature, the absolute and relative rate data of Perry et al. (1977), Atkinson et al. (1978), Atkinson and Aschmann (1990), Semadeni et al. (1995) and Coeur-Tourneur et al. (2006) are in agreement within the experimental uncertainties. The preferred values of *k* at ≤350 K are based on a least-squares analysis of the absolute rate coefficients of Perry et al. (1977) and the relative rate data of Atkinson and Aschmann (1990) [which is judged to supersede the earlier study of Atkinson et al. (1978)], Semadeni et al. (1995) and Coeur-Tourneur et al. (2006). Note that no rate coefficients have been measured below 294 K. Furthermore, the rate coefficients used to derive the preferred temperature dependence may have been influenced by fall-off effects and/or thermal decomposition of the HO-cresol adducts, and hence the preferred rate expression should not be used below ~290 K.

The rate coefficients of Perry et al. (1977) at 400-423 K suggest that H-atom abstraction, attributed to (k_1 + k_2), is minor at room temperature and below, accounting for ~6% of the overall reaction at 298 K to within a factor of ~2 using the Perry et al. (1977) fit to their 400-423 K data. The values of (k_1 + k_2) of Perry et al. (1977) at ~400 K are factors of ~200 and ~10 higher than the rate coefficients for H-atom abstraction from the ring C-H bonds in benzene and from the C-H bonds in the CH_3 substituent group in toluene, respectively (Knispel et al., 1990; IUPAC, 2019), indicating that for HO + *o*-cresol channel (1) dominates over channel (2) (i.e., $k_1 > k_2$). Moreover, the values of $(k_1 + k_2)$ of Perry et al. (1977) for HO + *o*-cresol at ~400 K are similar to those of Knispel et al. (1990) for HO + phenol at 354 K and 374 K, again consistent with H-atom abstraction from the OH group dominating over H-atom abstraction from the ring C-H bonds or the C-H bonds of the CH_3 group.

At atmospherically-relevant temperatures, the reaction therefore proceeds almost entirely by channels (1) and (3), with channel (1) accounting for ~$(6\ ^{+6}_{-3})$% of the overall reaction at 298 K and for less at lower temperatures. In the presence of NO_x, Atkinson et al. (1992), Olariu et al. (2002) and Coeur-Tourneur et al. (2006) measured 6-methyl-2-nitrophenol formation yields from the OH radical-initiated reaction of *o*-cresol to be 5.1 ± 1.5% at 296 ± 2 K, 6.8 ± 1.5% at 298 ± 2 K, and 4.7 ± 0.8% at 294 ± 2 K, respectively. Since 6-methyl-2-nitrophenol formation is attributed to the reaction of 2-methylphenoxy radicals with NO_2, these observations indicate that at room temperature channel (1) accounts for least 5% of the overall reaction, consistent with the kinetic data.

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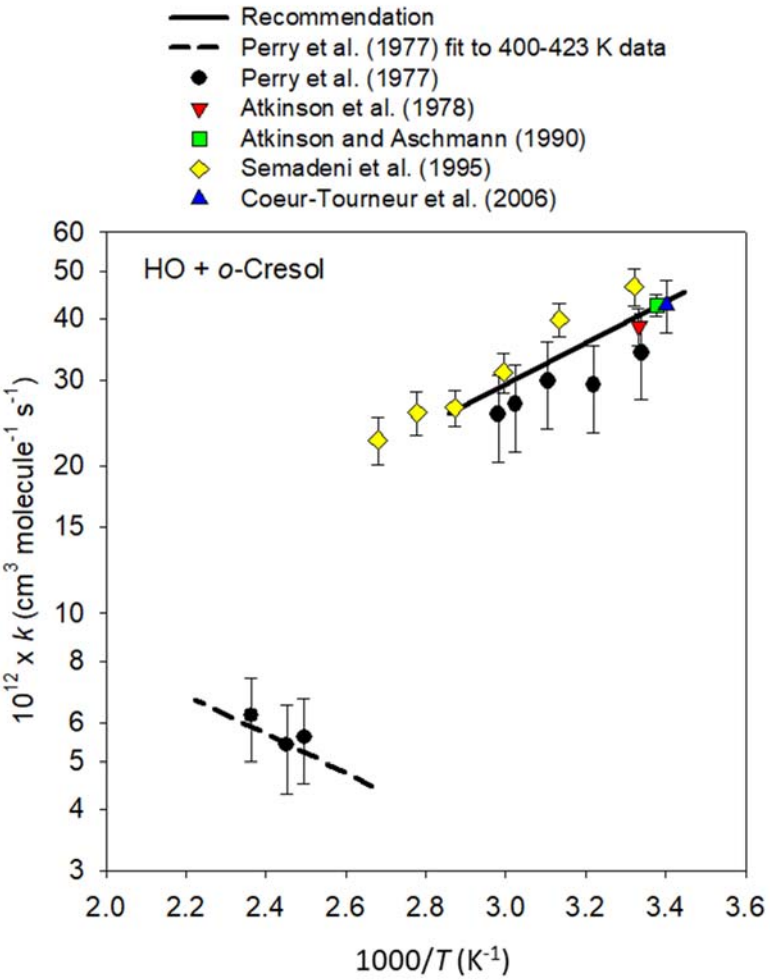

Rate coefficients for HO + *o*-cresol.

HOx_AROM5: *p*-cresol

Last evaluated: September 2008; Last change in preferred values: September 2008

$$\mathbf{HO + \mathit{p}\text{-}CH_3C_6H_4OH \rightarrow H_2O + CH_3C_6H_4O} \quad \mathbf{(1)}$$

$$\mathbf{\rightarrow H_2O + CH_2C_6H_4OH} \quad \mathbf{(2)}$$

$$\mathbf{\rightarrow CH_3C_6H_4(OH)_2} \quad \mathbf{(3)}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(4.47 \pm 0.21) \times 10^{-11}$	300 ± 1	Atkinson et al., 1978	RR (a)
$(5.24 \pm 0.51) \times 10^{-11}$	296 ± 2	Atkinson and Aschmann, 1990	RR (b)
$1.12 \times 10^{-12} \exp[(1180.4 \pm 444.5)/T]$	301-373	Semadeni et al., 1995	RR (c)
$(5.42 \pm 0.54) \times 10^{-11}$	301		
$(4.38 \pm 0.69) \times 10^{-11}$	301	Semadeni et al., 1995	RR (d)
$(4.53 \pm 0.39) \times 10^{-11}$	314		
$(4.88 \pm 0.74) \times 10^{-11}$	294 ± 2	Coeur-Tourneur et al., 2006	RR (e)

Comments

(a) HO radicals were generated by the photolysis of NO_x-organic-air mixtures in a ~5500 L Teflon chamber at wavelengths >300 nm at atmospheric pressure. The concentrations of *p*-cresol and *o*-cresol (the reference organics) were measured by GC. The measured rate coefficient ratio k(HO + *p*-cresol)/k(HO + *o*-cresol) = 1.10 ± 0.05 is placed on an absolute basis using a rate coefficient at 300 K of k(HO + *o*-cresol) = 4.06×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(b) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure. The concentrations of *p*-cresol and propene (the reference compound) were monitored by GC. The measured rate coefficient ratio k(HO + *p*-cresol)/k(HO + propene) = 2.55 ± 0.15 is placed on an absolute basis using k(HO + propene) = 2.88×10^{-11} cm^3 molecule^{-1} s^{-1} at 296 K and atmospheric pressure of air (IUPAC, 2019).

(c) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Teflon chamber. *p*-Cresol and 1,3-butadiene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + *p*-cresol)/k(HO + 1,3-butadiene) = $0.076 \exp[(732.4 \pm 444.5)/T]$ over the temperature range 301-373 K is placed on an absolute basis using k(HO + 1,3-butadiene) = $1.48 \times 10^{-11} \exp(448/T)$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(d) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Teflon chamber. *p*-Cresol and *o*-cresol (the reference compound) were monitored by GC, and the measured rate coefficient ratios k(HO + *p*-cresol)/k(HO + *o*-cresol) = 1.09 ± 0.17 at 301 K and 1.29 ± 0.11 at 314 K are placed on an absolute basis using k(HO + *o*-cresol) = $1.6 \times 10^{-12} \exp(970/T)$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(e) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~8000 L Plexiglas chamber. *p*-Cresol and 1,3,5-trimethylbenzene (the reference compound) were monitored by GC, and the measured rate coefficient ratios k(HO + *p*-cresol)/k(HO +

1,3,5-trimethylbenzene) = 0.86 ± 0.13 is placed on an absolute basis using k(HO + 1,3,5-trimethylbenzene) = 5.67×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	4.8×10^{-11}	298
k /cm^3 $molecule^{-1}$ s^{-1}	$1.9 \times 10^{-12} \exp(970/T)$	290-350
Reliability		
$\Delta \log k$	± 0.10	298
Δ E/R	± 600	290-350

Comments on Preferred Values

As for the reactions of HO radicals with benzene, toluene, phenol and *o*-cresol (IUPAC, 2019), the reaction of HO radicals with *p*-cresol can be considered as comprising three temperature regimes. At temperatures <325-350 K the reaction proceeds by channels (1-3), with pathway (3) dominating and with the HO-cresol adducts being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (based on the analogous HO + phenol reaction (IUPAC, 2019)). At temperatures >400-450 K, decomposition of the HO-cresol adducts back to reactants is sufficiently rapid that measured rate coefficients are then those for pathway (1) and (2). At temperatures in the range ~325-400 K, decomposition of the HO-cresol adducts is significant and the measured rate coefficients depend on the experimental conditions.

The available rate coefficients (Atkinson et al., 1978; Atkinson and Aschmann, 1990; Semadeni et al., 1995; Coeur-Tourneur et al., 2006) are all from relative rate studies, with only one study being carried out as a function of temperature (Semadeni et al., 1995). At room temperature, the relative rate data of Atkinson et al. (1978), Atkinson and Aschmann (1990), Semadeni et al. (1995) and Coeur-Tourneur et al. (2006) are in reasonable agreement. The temperature dependence obtained from the Semadeni et al. (1995) study (using rate coefficients at <350 K) has a large uncertainty, but is generally similar to those for HO + *o*-cresol (E/R = -970 K) and HO + *m*-cresol (E/R = -965 K) (IUPAC, 2019). Accordingly, a temperature dependence equal to that for the HO + *o*-cresol reaction is used. The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Atkinson and Aschmann (1990) [which is judged to supersede the earlier study of Atkinson et al. (1978)], Semadeni et al. (1995) [using only the rate coefficient measured relative to 1,3-butadiene] and Coeur-Tourneur et al. (2006), using the preferred temperature dependence to correct the measured rate coefficients to 298 K. The pre-exponential factor is adjusted to fit the 298 K preferred value. Note that no rate coefficients have been measured below 294 K. Furthermore, the rate coefficients used to derive the preferred temperature dependence may have been influenced by thermal decomposition of the HO-cresol adducts, and hence the preferred rate expression should not be used below ~290 K

By analogy with the HO + *o*-cresol reaction (Perry et al., 1977; IUPAC, 2019), at atmospherically-relevant temperatures the HO + *p*-cresol reaction is expected to proceed almost entirely by channels (1) and (3), with channel (1) accounting for a minor fraction (~5%) of the overall reaction at 298 K and for less at lower temperatures. In the presence of NO_x, Atkinson et al. (1992), Olariu et al. (2002) and Coeur-Tourneur et al. (2006) measured 4-methyl-2-nitrophenol formation yields from the HO radical-initiated reaction of *o*-cresol to be 10 ± 4%

at 296 ± 2 K, 7.6 ± 2.2% at 298 ± 2 K, and 17.2 ± 2.5% at 294 ± 2 K, respectively. Since 4-methyl-2-nitrophenol formation is attributed to the reaction of 2-methylphenoxy radicals with NO_2, these observations indicate that at room temperature channel (1) accounts for least 5-6% of the overall reaction, reasonably consistent with the approximate estimate from kinetic data from the *o*- and *p*-cresol reactions.

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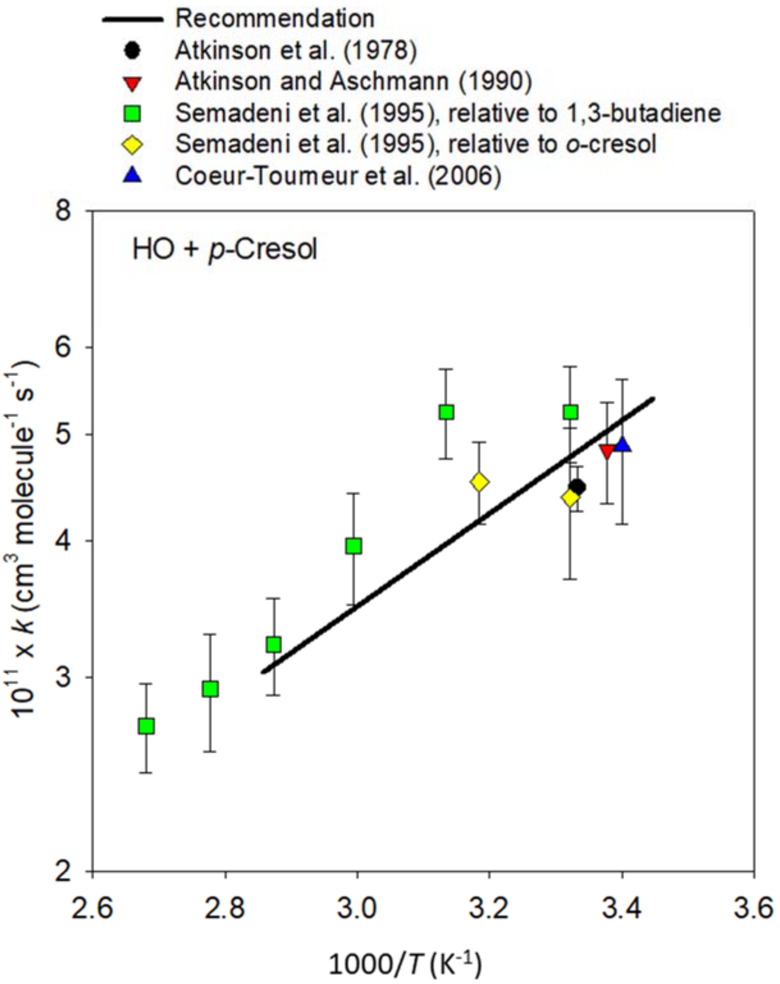

Rate coefficients for HO + *p*-cresol.

HOx_AROM6: phenol

Last evaluated: September 2008; Last change in preferred values: September 2008

$HO + C_6H_5OH$	$\rightarrow H_2O + C_6H_5O$	**(1)**
	$\rightarrow H_2O + C_6H_4OH$	**(2)**
	$\rightarrow HOC_6H_5OH$	**(3)**

Rate coefficient data ($k = k_1 + k_2 + k_3$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.83 \pm 0.57) \times 10^{-11}$	296	Rinke and Zetzsch, 1984	FP-RF (a)
$k_1 + k_2 = (0 \pm 0.5) \times 10^{-12}$	300	Knispel et al., 1990	FP-RF (b)
$k_3 = (2.9 \pm 0.3) \times 10^{-11}$	300		
$k_1 + k_2 = (0 \pm 0.5) \times 10^{-12}$	308		
$k_3 = (2.6 \pm 0.3) \times 10^{-11}$	308		
$k_1 + k_2 = (3.4 \pm 0.5) \times 10^{-12}$	323		
$k_3 = (1.9 \pm 0.2) \times 10^{-11}$	323		
$k_1 + k_2 = (4.6 \pm 0.5) \times 10^{-12}$	339		
$k_3 = (1.4 \pm 0.2) \times 10^{-11}$	339		
$k_1 + k_2 = (4.6 \pm 0.4) \times 10^{-12}$	354		
$k_3 = (1.3 \pm 0.2) \times 10^{-11}$	354		
$k_1 + k_2 = (5.1 \pm 0.4) \times 10^{-12}$	374		
$k_3 = (1.2 \pm 0.2) \times 10^{-11}$	374		
Relative Rate Cofficients			
1.35×10^{-11}	1032	He et al., 1988	RR (c)
$2.66 \times 10^{-13} \exp[(1376.5 \pm 282.5)/T]$	301-373	Semadeni et al., 1995	RR (d)
$(2.56 \pm 0.27) \times 10^{-11}$	301		
$(2.41 \pm 0.21) \times 10^{-11}$	301	Semadeni et al., 1995	RR (e)
$(2.07 \pm 0.18) \times 10^{-11}$	314		

Comments

(a) Rate coefficients were measured over the pressure range 5-733 mbar (3.75-550 Torr) of He diluent, with no effect of pressure on the rate coefficient being observed at pressures ≥43 mbar (32 Torr). The cited rate coefficient is at 133 mbar pressure.

(b) Rate coefficients k_1 and k_2 were derived from fitting the observed biexponential HO radical decays, measured at a total pressure of 133 mbar of Ar, to reactions (1) plus (2), (3), the back-decomposition of the HO-phenol adducts and accounting for diffusive and background losses of HO radicals and the HO-phenol adducts. Using the rate coefficient of He et al. (1988) at 1032 K and the expression $(k_1 + k_2) = C\,T^2 \exp(-D/T)$, a global fit to the experimental data resulted in rate coefficients $(k_1 + k_2)$ of $(3.97 \pm 0.03) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, essentially independent of temperature, over the range 300-374 K.

(c) Based on the effect of added CO on shocked 2,2,3,3-tetramethylbutane-phenol-Ar mixtures. The derived rate coefficient ratio $k(HO + \text{phenol})/k(HO + CO) = 33.2$ (from the listed rate expressions) is placed on an absolute basis by use of $k(HO + CO) = 4.08 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 1032 K and 3.75 ± 1.25 bar pressure (Atkinson, 2003). From comparison of their rate coefficient at 1032 K with those of Tully et al. (1981) for HO + benzene at ~1000 K, He et al. (1988) concluded that channel (1) was the dominant reaction pathway.

(d) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Teflon chamber. Phenol and 1,3-butadiene (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + phenol)/k(HO + 1,3-butadiene) = 0.018 exp[(925.5 ± 282.5)/T] over the temperature range 301-373 K is placed on an absolute basis using a rate coefficient of k(HO + 1,3-butadiene) = $1.48 \times 10^{-11} \exp(448/T)$ cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003).

(e) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Teflon chamber. Phenol and *o*-cresol (the reference compound) were monitored by GC, and the measured rate coefficient ratios k(HO + phenol)/k(HO + *o*-cresol) = 0.60 ± 0.05 at 301 K and 0.59 ± 0.05 at 314 K are placed on an absolute basis using a rate coefficient of k(HO + o-cresol) = $1.6 \times 10^{-12} \exp(970/T)$ cm^3 $molecule^{-1}$ s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	2.8×10^{-11}	298
k /cm^3 $molecule^{-1}$ s^{-1}	$4.7 \times 10^{-13} \exp(1220/T)$	290-350
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 600	290-350

Comments on Preferred Values

As for the reactions of HO radicals with benzene and toluene (IUPAC, 2019), the reaction of HO radicals with phenol can be considered as comprising three temperature regimes. At temperatures <325-350 K the reaction proceeds by channels (1-3), with pathway (3) dominating and with the HO-phenol adduct, HOC_6H_5OH, being thermally stable against back-decomposition to reactants at total pressures above ~30 Torr (Rinke and Zetzsch, 1984). At temperatures >400-450 K, decomposition of the HO-phenol adduct back to reactants is sufficiently rapid that measured rate coefficients are then those for pathways (1) and/or (2). At temperatures in the range ~325-450 K, decomposition of the HO-phenol adduct is significant and the measured rate coefficients depend on the experimental conditions.

The preferred values of k at ≤350 K are based on the absolute rate coefficients of Rinke and Zetzsch (1984) and Knispel et al. (1990) and the rate coefficients measured by Semadeni et al. (1995) relative to 1,3-butadiene. The rate coefficients measured by Semadeni et al. (1995) relative to *o*-cresol at 301 K and 314 K are in good agreement with the preferred values, indicating that the preferred values for HO + phenol and HO + *o*-cresol (IUPAC, 2019) are internally self-consistent. Note that no rate coefficients have been measured below 296 K. Furthermore, the rate coefficients used to derive the preferred temperature dependence may have been influenced by fall-off effects and/or thermal decomposition of the HO-phenol adducts, and hence the preferred rate expression should not be used below ~290 K.

An Arrhenius fit to the relative rate coefficient of He et al. (1988) at 1032 K (which is subject to significant uncertainty, in part due to uncertainties in the rate coefficient for the reaction of HO radicals with CO, the reference compound used) and the values of (k_1 + k_2)

derived by Knispel et al. (1990) from HO radical decay curves at 323 K, 339 K, 354 K and 374 K results in (k_1 + k_2) ~ 2.4 × 10^{-11} exp(-590/T) cm^3 $molecule^{-1}$ s^{-1}. The values of (k_1 + k_2) obtained by Knispel et al. (1990) at ~350 K are a factor of ~200 higher than the rate coefficient for H-atom abstraction from the ring C-H bonds in benzene (Knispel et al., 1990; IUPAC, 2019), indicating that for HO + phenol channel (1) dominates over channel (2) (i.e., $k_1 >> k_2$). Hence, as also concluded by He et al. (1988), channel (2) is of no importance and can be neglected at temperatures <1100 K.

At atmospherically-relevant temperatures, the reaction proceeds almost entirely by channels (1) and (3), with channel (1) being estimated to account for ~12% of the overall reaction of HO radicals with phenol at 298 K, and for less at lower temperatures. In the presence of NO_x, Atkinson et al. (1992) and Olariu et al. (2002) measured 2-nitrophenol formation yields from the HO radical-initiated reaction of phenol to be 6.7 ± 1.5% at 296 ± 2 K and 5.8 ± 1.0% at 298 ± 2 K, respectively. Since 2-nitrophenol formation is attributed to the reaction of phenoxy radicals with NO_2, these observations indicate that at room temperature channel (1) accounts for least 6% of the overall reaction, consistent with the kinetic data.

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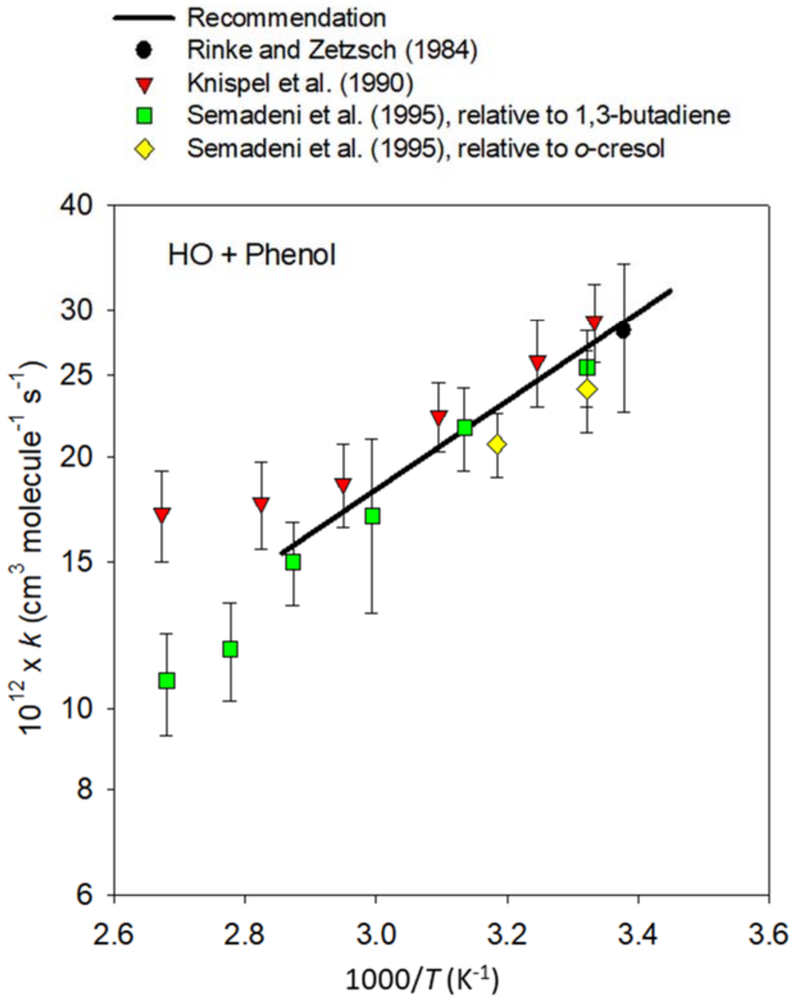
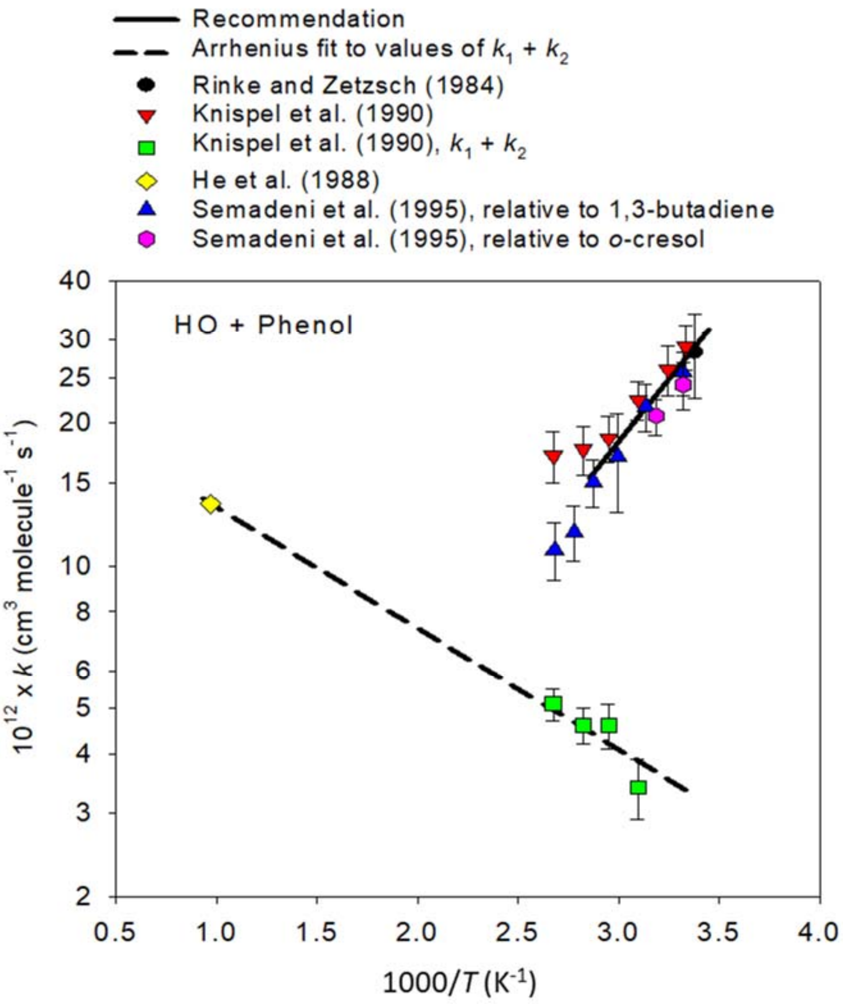


Rate coefficients for HO + phenol.



Rate coefficients for HO + phenol.

HOx_AROM7: 1,2-dihydroxybenzene

Last evaluated: November 2008; Last change in preferred values: November 2008

$HO + 1,2\text{-}C_6H_4(OH)_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.01 \pm 0.04) \times 10^{-10}$	300 ± 5	Olariu et al., 2000	RR (a,b)
$(1.06 \pm 0.04) \times 10^{-10}$	300 ± 5	Olariu et al., 2000	RR (a,c)
$(1.01 \pm 0.04) \times 10^{-10}$	300 ± 5	Olariu et al., 2000	RR (a,d)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 1,2-dihydroxybenzene and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxybenzene were measured and taken into account in the data analysis, and these contributed ~30% of the 1,2-dihydroxybenzene loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of k(HO + 1,2-dihydroxybenzene)/k(HO + isoprene) = 1.024 ± 0.04, k(HO + 1,2-dihydroxybenzene)/k(HO + 1,3-butadiene) = 1.608 ± 0.052 and k(HO + 1,2-dihydroxybenzene)/k(HO + *trans*-2-butene) = 1.606 ± 0.05 are placed on an absolute basis using rate coefficients at 300 K of k(HO + isoprene) = 9.91×10^{-11} (IUPAC, 2019), k(HO + 1,3-butadiene) = 6.59×10^{-11} (Atkinson and Arey, 2003) and k(HO + *trans*-2-butene) = 6.32×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) Relative to k(HO + isoprene).

(c) Relative to k(HO + 1,3-butadiene).

(d) Relative to k(HO + *trans*-2-butene).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-10}	298
Reliability		
$\Delta \log k$	±0.15	298

Comments on Preferred Values

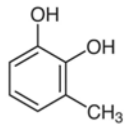
The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

Reference

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

HOx_AROM8: 1,2-dihydroxy-3-methylbenzene

Last evaluated: November 2008; Last change in preferred values: November 2008

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.90 \pm 0.07) \times 10^{-10}$	300 ± 5	Olariu et al., 2000	RR (a,b)
$(1.99 \pm 0.06) \times 10^{-10}$	300 ± 5	Olariu et al., 2000	RR (a,c)
$(1.99 \pm 0.07) \times 10^{-10}$	300 ± 5	Olariu et al., 2000	RR (a,d)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 1,2-dihydroxy-3-methylbenzene and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-3-methylbenzene were measured and taken into account in the data analysis, and these contributed ~30% of the 1,2-dihydroxy-3-methylbenzene loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of k(HO + 1,2-dihydroxy-3-methylbenzene)/k(HO + isoprene) = 1.92 ± 0.07, k(HO + 1,2-dihydroxy-3-methylbenzene)/k(HO + 1,3-butadiene) = 3.02 ± 0.09 and k(HO + 1,2-dihydroxy-3-methylbenzene)/k(HO + *trans*-2-butene) = 3.15 ± 0.1 are placed on an absolute basis by use of rate coefficients at 300 K of k(HO + isoprene) = 9.91×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019), k(HO + 1,3-butadiene) = 6.59×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) and k(HO + *trans*-2-butene) = 6.32×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) Relative to k(HO + isoprene).

(c) Relative to k(HO + 1,3-butadiene).

(d) Relative to k(HO + *trans*-2-butene).

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	2.0×10^{-10}	298
Reliability		
$\Delta \log k$	±0.15	298

Comments on Preferred Values

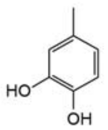
The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

HOx_AROM9: 1,2-dihydroxy-4-methylbenzene

Last evaluated: November 2008; Last change in preferred values: November 2008

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.60 \pm 0.08) \times 10^{-10}$	300 ± 5	Olariu et al., 2000	RR (a,b)
$(1.52 \pm 0.04) \times 10^{-10}$	300 ± 5	Olariu et al., 2000	RR (a,c)
$(1.50 \pm 0.03) \times 10^{-10}$	300 ± 5	Olariu et al., 2000	RR (a,d)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 1,2-dihydroxy-4-methylbenzene and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-4-methylbenzene were measured and taken into account in the data analysis, and these contributed ~30% of the 1,2-dihydroxy-4-methylbenzene loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of k(HO + 1,2-dihydroxy-4-methylbenzene)/k(HO + isoprene) = 1.61 ± 0.072, k(HO + 1,2-dihydroxy-4-methylbenzene)/k(HO + 1,3-butadiene) = 2.31 ± 0.048 and k(HO + 1,2-dihydroxy-4-methylbenzene)/k(HO + *trans*-2-butene) = 2.37 ± 0.047 are placed on an absolute basis by use of rate coefficients at 300 K of k(HO + isoprene) = 9.91×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019), k(HO + 1,3-butadiene) = 6.59×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) and k(HO + *trans*-2-butene) = 6.32×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) Relative to k(HO + isoprene).

(c) Relative to k(HO + 1,3-butadiene).

(d) Relative to k(HO + *trans*-2-butene).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.5×10^{-10}	298
Reliability		
$\Delta \log k$	±0.15	298

Comments on Preferred Values

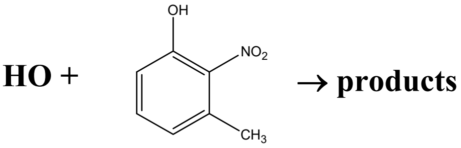
The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

HOx_AROM10: 3-methyl-2-nitrophenol

Last evaluated: November 2008; Last change in preferred values: November 2008



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(3.39 \pm 0.18) \times 10^{-12}$	296 ± 3	Bejan et al., 2007	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 3-methyl-2-nitrophenol and ethene (the reference compound) were measured by FTIR spectroscopy. Wall losses and photolysis of 3-methyl-2-nitrophenol were measured and taken into account in the data analysis, and these contributed ~50-55% of the total measured 3-methyl-2-nitrophenol loss rate during the experiments. The measured rate coefficient ratio of k(HO + 3-methyl-2-nitrophenol)/k(HO + ethene) = 0.43 ± 0.02 is placed on an absolute basis by use of a rate coefficient at 296 K and atmospheric pressure of air of k(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.4×10^{-12}	298
Reliability		
$\Delta \log k$	±0.30	298

Comments on Preferred Values

The 298 K preferred value is based on the sole reported study of Bejan et al. (2007).

References

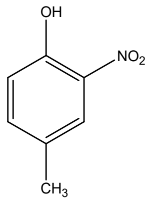
Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P. and Benter, Th.: Phys. Chem. Chem. Phys., 9, 5686, 2007.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_AROM11: 4-methyl-2-nitrophenol

Last evaluated: November 2008; Last change in preferred values: November 2008

HO +



→ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(3.19 \pm 0.18) \times 10^{-12}$	296 ± 3	Bejan et al., 2007	RR (a,b)
$(3.60 \pm 0.54) \times 10^{-12}$	296 ± 3	Bejan et al., 2007	RR (a,c)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 4-methyl-2-nitrophenol and ethene or *n*-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses and photolysis of 4-methyl-2-nitrophenol were measured and taken into account in the data analysis, and these contributed ~50-55% of the total measured 4-methyl-2-nitrophenol loss rate during the experiments. The measured rate coefficient ratios of k(HO + 4-methyl-2-nitrophenol)/k(HO + ethene) = 0.41 ± 0.02 and k(HO + 4-methyl-2-nitrophenol)/k(HO + *n*-butane) = 1.55 ± 0.23 are placed on an absolute basis by use of rate coefficients at 296 K and atmospheric pressure of air of k(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019) and k(HO + *n*-butane) = 2.32×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(b) Relative to k(HO + ethene).

(c) Relative to k(HO + *n*-butane).

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	3.4×10^{-12}	298
Reliability		
$\Delta \log k$	±0.15	298

Comments on Preferred Values

The rate coefficients measured by Bejan et al. (2007) at 296 ± 3 K using a relative rate method with two different reference compounds are in good agreement. The 298 K preferred value is an un-weighted average of the two values of Bejan et al. (2007). The assigned uncertainty reflects the fact that all of the data are from a single study and the need to account for significant wall losses and photolysis of the 4-methyl-2-nitrophenol.

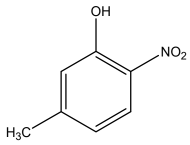
References

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P. and Benter, Th.: Phys. Chem. Chem. Phys., 9, 5686, 2007.

HOx_AROM12: 5-methyl-2-nitrophenol

Last evaluated: November 2008; Last change in preferred values: November 2008

HO +



→ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(5.15 \pm 0.35) \times 10^{-12}$	296 ± 3	Bejan et al., 2007	RR (a,b)
$(7.60 \pm 1.56) \times 10^{-12}$	296 ± 3	Bejan et al., 2007	RR (a,c)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 5-methyl-2-nitrophenol and ethene or *n*-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses and photolysis of 5-methyl-2-nitrophenol were measured and taken into account in the data analysis, and these contributed 29-33% of the total measured 5-methyl-2-nitrophenol loss rate during the experiments. The measured rate coefficient ratios of k(HO + 5-methyl-2-nitrophenol)/k(HO + ethene) = 0.67 ± 0.04 and k(HO + 5-methyl-2-nitrophenol)/k(HO + *n*-butane) = 3.274 ± 0.67 (the rate coefficient ratio cited in Bejan et al. (2007) is in error (I. Barnes, private communication, 2008)) are placed on an absolute basis by use of rate coefficients at 296 K and atmospheric pressure of air of k(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019) and k(HO + *n*-butane) = 2.32×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(b) Relative to k(HO + ethene).

(c) Relative to k(HO + *n*-butane).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	6.4×10^{-12}	298
Reliability		
$\Delta \log k$	±0.20	298

Comments on Preferred Values

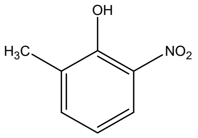
The rate coefficients measured by Bejan et al. (2007) at 296 ± 3 K using a relative rate method with two different reference compounds disagree by ≈30%. The 298 K preferred value is an un-weighted average of the two values of Bejan et al. (2007). The assigned uncertainty reflects the fact that all of the data are from a single study and the need to account for significant wall losses and photolysis of the 5-methyl-2-nitrophenol.

References

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P. and Benter, Th.: Phys. Chem. Chem. Phys., 9, 5686, 2007.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_AROM13: 6-methyl-2-nitrophenol

Last evaluated: November 2008; Last change in preferred values: November 2008

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(2.49 \pm 0.18) \times 10^{-12}$	296 ± 3	Bejan et al., 2007	RR (a)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 6-methyl-2-nitrophenol and ethene (the reference compound) were measured by FTIR spectroscopy. Wall losses and photolysis of 6-methyl-2-nitrophenol were measured and taken into account in the data analysis, and these contributed ~50-55% of the total measured 6-methyl-2-nitrophenol loss rate during the experiments. The measured rate coefficient ratio of k(HO + 6-methyl-2-nitrophenol)/k(HO + ethene) = 0.32 ± 0.02 is placed on an absolute basis by use of a rate coefficient at 296 K and atmospheric pressure of air of k(HO + ethene) = 7.78×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.5×10^{-12}	298
Reliability		
$\Delta \log k$	±0.30	298

Comments on Preferred Values

The 298 K preferred value is based on the sole reported study of Bejan et al. (2007).

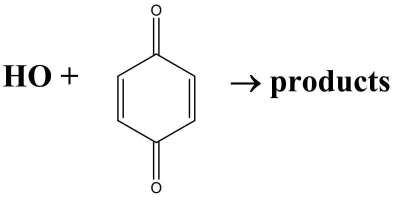
References

Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P. and Benter, Th.: Phys. Chem. Chem. Phys., 9, 5686, 2007.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_AROM14: 1,4-benzoquinone

Last evaluated: November 2008; Last change in preferred values: November 2008



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(4.66 \pm 0.10) \times 10^{-12}$	300 ± 5	Olariu et al., 2000	RR (a,b)
$(4.55 \pm 0.14) \times 10^{-12}$	300 ± 5	Olariu et al., 2000	RR (a,c)
$(4.61 \pm 0.13) \times 10^{-12}$	300 ± 5	Olariu et al., 2000	RR (a,d)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of 1,4-benzoquinone and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,4-benzoquinone were measured and taken into account in the data analysis, and these contributed ~30% of the 1,4-benzoquinone loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of k(HO + 1,4-benzoquinone)/k(HO + isoprene) = 0.047 ± 0.001, k(HO + 1,4-benzoquinone)/k(HO + 1,3-butadiene) = 0.069 ± 0.002 and k(HO + 1,4-benzoquinone)/k(HO + *trans*-2-butene) = 0.073 ± 0.002 are placed on an absolute basis by use of rate coefficients at 300 K of k(HO + isoprene) = 9.91×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019), k(HO + 1,3-butadiene) = 6.59×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) and k(HO + *trans*-2-butene) = 6.32×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) Relative to k(HO + isoprene).

(c) Relative to k(HO + 1,3-butadiene).

(d) Relative to k(HO + *trans*-2-butene).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	4.6×10^{-12}	298
Reliability		
$\Delta \log k$	±0.15	298

Comments on Preferred Values

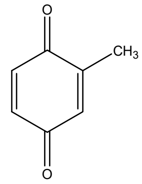
The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

HOx_AROM15: methyl-1,4-benzoquinone

Last evaluated: November 2008; Last change in preferred values: November 2008

HO +  → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(2.28 \pm 0.10) \times 10^{-11}$	300 ± 5	Olariu et al., 2000	RR (a,b)
$(2.37 \pm 0.07) \times 10^{-11}$	300 ± 5	Olariu et al., 2000	RR (a,c)
$(2.34 \pm 0.07) \times 10^{-11}$	300 ± 5	Olariu et al., 2000	RR (a,d)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO. Experiments were carried out in a 1080 L chamber at 1.013 bar of air. The concentrations of methyl-1,4-benzoquinone and isoprene, 1,3-butadiene or *trans*-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of methyl-1,4-benzoquinone were measured and taken into account in the data analysis, and these contributed ~30% of the methyl-1,4-benzoquinone loss rate due to HO radical reaction during the experiments. The measured rate coefficient ratios of k(HO + methyl-1,4-benzoquinone)/k(HO + isoprene) = 0.23 ± 0.01, k(HO + methyl-1,4-benzoquinone)/k(HO + 1,3-butadiene) = 0.36 ± 0.01 and k(HO + methyl-1,4-benzoquinone)/k(HO + *trans*-2-butene) = 0.37 ± 0.01 are placed on an absolute basis by use of rate coefficients at 300 K of k(HO + isoprene) = 9.91×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019), k(HO + 1,3-butadiene) = 6.59×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) and k(HO + *trans*-2-butene) = 6.32×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) Relative to k(HO + isoprene).

(c) Relative to k(HO + 1,3-butadiene).

(d) Relative to k(HO + *trans*-2-butene).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.3×10^{-11}	298
Reliability		
$\Delta \log k$	±0.15	298

Comments on Preferred Values

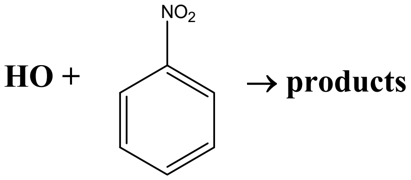
The three rate coefficients measured by Olariu et al. (2000) at 300 ± 5 K using a relative rate method with three different reference compounds are in excellent agreement. The 298 K preferred value is an average of the three values of Olariu et al. (2000). The assigned uncertainty reflects the fact that all of the data are from a single study.

References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Olariu, R. I., Barnes, I., Becker, K. H. and Klotz, B.: Int. J. Chem. Kinet., 32, 696, 2000.

HOx_AROM16: nitrobenzene

Last evaluated: November 2008; Last change in preferred values: November 2008



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$6 \times 10^{-13} \exp[-(440 \pm 80)/T]$	259-362	Witte et al., 1986	FP-RF (a)
$(1.37 \pm 0.14) \times 10^{-13}$	299		
Relative Rate Cofficients			
$<6.4 \times 10^{-13}$	296 ± 2	Atkinson et al., 1987	RR (b)
$<8.3 \times 10^{-13}$	296 ± 2	Atkinson et al., 1987	RR (c)

Comments

(a) At 100 Torr (133 mbar) of Ar diluent.

(b) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~60 L Teflon chamber, with analyses of nitrobenzene and benzene (the reference compound) by GC. The measured rate coefficient ratio k(HO + nitrobenzene)/k(HO + benzene) <0.53 is placed on an absolute basis using a rate coefficient of k(HO + benzene) = 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, 2019).

(c) HO radicals generated by the dark reaction of $O_3 + N_2H_4$ in air at atmospheric pressure in a 5870 L reaction chamber. The concentrations of nitrobenzene and dimethyl ether (the reference compound) were monitored by FTIR spectroscopy, and the measured rate coefficient ratio k(HO + nitrobenzene)/k(HO + dimethyl ether) <0.3 is placed on an absolute basis using a rate coefficient of k(HO + dimethyl ether) = 2.76×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, 2019).

Preferred Values

Parameter	**Value**	***T*/K**
k /cm^3 molecule^{-1} s^{-1}	1.4×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$6.0 \times 10^{-13} \exp(-440/T)$	250-370
Reliability		
$\Delta \log k$	± 0.20	298
$\Delta E/R$	± 300	250-370

Comments on Preferred Values

The upper limits to the rate coefficients obtained by Atkinson et al. (1987) are consistent with the absolute rate coefficients measured by Witte et al. (1986). The rate expression reported by Witte et al. (1986) is accepted as the preferred value. Since the Witte et al. (1986) study is the sole published study to report rate coefficients for this reaction (rather than upper limits), correspondingly large uncertainties are given. The reaction proceeds mainly by HO radical addition to the aromatic ring (Witte et al., 1986).

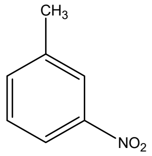
References

Atkinson, R., Tuazon, E. C., Wallington, T. J., Aschmann, S. M., Arey, J., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 21, 64, 1987.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Witte, F., Urbanik, E. and Zetzsch, C.: J. Phys. Chem., 90, 3251, 1986.

HOx_AROM17: 3-nitrotoluene

Last evaluated: November 2008; Last change in preferred values: November 2008

HO +



→ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.22 \pm 0.82) \times 10^{-12}$	298 ± 2	Atkinson et al., 1989	RR (a)

Comments

(a) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~6400 L Teflon chamber, with analyses of 3-nitrotoluene and benzene (the reference compound) by GC. The measured rate coefficient ratio k(HO + nitrobenzene)/k(HO + benzene) = 1.02 ± 0.68 is placed on an absolute basis using a rate coefficient of k(HO + benzene) = 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.2×10^{-12}	298
Reliability		
$\Delta \log k$	±0.50	298

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study reported to date.

References

Atkinson, R., Aschmann, S. M., Arey, J. and Carter, W. P. L.: Int. J. Chem. Kinet., 21, 801, 1989.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_AROM18: *cis*-butene-2-dial

Last evaluated: June 2009; Last change in preferred values: June 2009

HO + *cis*-CHOCH=CHCHO → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(5.73 \pm 0.12) \times 10^{-11}$	296 ± 2	Bierbach et al., 1994	RR-FTIR (a)

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of *cis*-butene-2-dial and propene (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm^{-1}. The measured rate coefficient ratio of k(HO + *cis*-butene-2-dial)/k(HO + propene) = 1.99 ± 0.04 is placed on an absolute basis using k(HO + propene) = 2.88×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	5.7×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.20	298

Comments on Preferred Value

The preferred value is based on the sole study of Bierbach et al. (1994) in 1 bar of air. The reaction proceeds both by H-atom abstraction from the -CHO groups and via addition to the double bond. In their mechanistic study of the HO reaction with a mixture of *cis*/*trans*-butenedial isomers, Bierbach et al. (1994) have reported that slightly less than 50% of the reaction proceeds by H-atom abstraction from the aldehyde functional groups of butenedial leading to furan-2,5-dione (maleic anhydride). Glyoxal, expected to be major product of the HO addition, has been also observed as a reaction product but could not be quantified. The formation yield of 3*H*-furan-2-one was reported to be 4%.

References

Bierbach, A., Barnes, I., Becker, K. H. and Wiesen E.: Environ. Sci. Technol., 28, 715, 1994.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_AROM19: *trans*-butene-2-dial

Last evaluated: June 2009; Last change in preferred values: June 2009

HO + *trans*-CHOCH=CHCHO → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$\geq (2.67 \pm 0.87) \times 10^{-11}$	296 ± 2	Bierbach et al., 1994	RR-FTIR (a)

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of *trans*-butene-2-dial and propene (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm^{-1}. Because of difficulties in the analysis of the data caused by *trans*/*cis* isomerisation, only a lower limit for the rate coefficient ratio could be derived k(HO + trans-butene-2-dial)/k(HO + propene) ≥ 0.92. This ratio is placed on an absolute basis using k(HO + propene) = 2.88×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Value

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	$\geq 2 \times 10^{-11}$	298

Comments on Preferred Value

The preferred value is based on the lower limit derived from the study of Bierbach et al. (1994) in 1 bar of air.

The reaction proceeds both by H-atom abstraction from the -CHO groups and via addition to the double bond. In their mechanistic study of the OH reaction with a mixture of *cis*/*trans*-butene-2-dial isomers, Bierbach et al. (1994) have reported that slightly less than 50% of the reaction proceeds by H-atom abstraction from the aldehyde functional groups of butenedial leading to furan-2,5-dione (maleic anhydride). Glyoxal, expected to be major product of the OH addition, has been also observed as a reaction product but could not be quantified. The formation yield of 3*H*-furan-2-one was reported to be 4%.

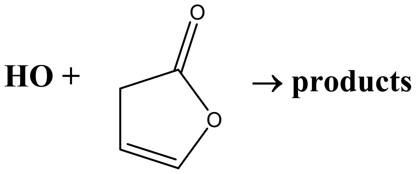
References

Bierbach, A., Barnes, I., Becker, K. H. and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_AROM20: 3*H*-furan-2-one

Last evaluated: June 2009; Last change in preferred values: June 2009



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(4.83 \pm 0.29) \times 10^{-11}$	296 ± 2	Bierbach et al., 1994	RR-FTIR (a)

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of 3H-furan-2-one and propene (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm^{-1}. The measured rate coefficient ratio of k(HO + 3H-furan-2-one)/k(HO + propene) = 1.68 ± 0.10 is placed on an absolute basis using k(HO + propene) = 2.88×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson et al., 2006).

Preferred Value

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	4.8×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.2	298

Comments on Preferred Value

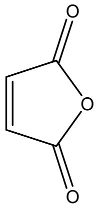
The preferred value is based on the sole study of Bierbach et al. (1994) in 1 bar of air but with higher uncertainty.

References

Bierbach, A., Barnes, I., Becker, K. H. and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_AROM21: furan-2,5-dione

Last evaluated: June 2009; Last change in preferred values: June 2009

HO +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.36 \pm 0.07) \times 10^{-12}$	296 ± 2	Bierbach et al., 1994	RR-FTIR (a)

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of furan-2,5-dione and n-butane (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm^{-1}. The measured rate coefficient ratio of k(HO + furan-2,5-dione)/k(HO + n-butane) = 0.58 ± 0.03 is placed on an absolute basis using k(HO + butane) = 2.35×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Value

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	1.4×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.20	298

Comments on Preferred Value

The preferred value is based on the sole study of Bierbach et al. (1994) in 1 bar of air.

Bierbach et al. (1994) conducted a product analysis of the HO-initiated oxidation of furan-2,5-dione (maleic anhydride) using either photolysis of H_2O_2 or CH_3ONO/NO/air as the HO source. CO (20% yield) and HCOOH (3% yield) were observed as reaction products using both sources. Acetylene (5%) was observed only with H_2O_2 as the HO source. CO_2 was reported a major reaction products but could not be quantified. The product IR spectra showed two carbonyl absorptions in the region 1820-1720 cm^{-1} but the identity of the compounds could not be determined. Bierbach et al. (1994) did not find evidence for the formation of PAN or other peroxynitrate type compounds.

References

Bierbach, A., Barnes, I., Becker, K. H. and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_AROM22: *cis-/trans*-4-oxopent-2-enal

Last evaluated: June 2009; Last change in preferred values: June 2009

HO + *cis/trans*-$CH_3C(O)CH=CHCHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(6.18 \pm 0.23) \times 10^{-11}$	296 ± 2	Bierbach et al., 1994	RR-FTIR (a)

Comments

(a) HO radicals were generated by the photolysis of H_2O_2 in 1000 mbar of air at $\lambda = 254$ nm. Experiments were carried out in a 1080-L quartz-glass chamber, and the concentrations of cis/*trans*-4-oxopent-2-enal and propene (the reference compound) were measured in situ by long-path FTIR using an optical path length of 492 m and a spectral resolution of 1 cm^{-1}. The measured rate coefficient ratio of k(HO + 4-oxopent-2-enal)/k(HO + propene) = 2.13 ± 0.08 is placed on an absolute basis using k(HO + propene) = 2.9×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Value

Parameter	Value	*T*/K
k /cm^3 molecule^{-1} s^{-1}	6.2×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.20	298

Comments on Preferred Value

The preferred value is based on the sole study of Bierbach et al. (1994) in 1 bar of air.

The reaction proceeds both by H-atom abstraction from the -CHO group and via addition to the double bond. Bierbach et al. (1994) reported that the HO reaction with a mixture of *cis*/*trans*-oxopent-2-enal isomers leading to formation of furan-2,5-dione (maleic anhydride) in a 40% yield which was taken as an indication that the abstraction channel plays an important role. Bierbach et al. (1994) also observed, but were not able to quantify, the formation of glyoxal and methylglyoxal which are expected to be major products following HO addition to the >C=C< double bond. The formation yield of 5-methyl-3*H*-furanone was reported to be 1%.

References

Bierbach, A., Barnes, I., Becker, K. H. and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

HOx_AROM25: benzaldehyde

Last evaluated: June 2009; Last change in preferred values: June 2009

$HO + C_6H_5CHO \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Cofficients			
$(1.26 \pm 0.08) \times 10^{-11}$	298 ± 2	Niki et al., 1978	RR (a, f)
$(1.1 \pm 0.2) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981	RR (b, f)
$5.7 \times 10^{-12} \exp[(225 \pm 57)/T)]$	294-343	Semadeni et al., 1995	RR (c, g)
$(1.22 \pm 0.07) \times 10^{-11}$	299		
$(1.20 \pm 0.14) \times 10^{-11}$	298 ± 2	Thiault et al., 2002	RR (d, g)
$(1.12 \pm 0.16) \times 10^{-11}$	298 ± 2	Thiault et al., 2002	RR (d, h)
$(1.15 \pm 0.13) \times 10^{-11}$	298 ± 2	Thiault et al., 2002	RR (d, i)
$(1.30 \pm 0.07) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, g)
$(1.31 \pm 0.12) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, j)
$(1.36 \pm 0.04) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, k)
$(1.46 \pm 0.20) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, l)
$(1.44 \pm 0.07) \times 10^{-11}$	295 ± 2	Clifford et al., 2005	RR (e, m)

Comments

(a) HO radicals were generated by the photolysis of HONO in air at atmospheric pressure in a 70 L Pyrex chamber. The concentrations of benzaldehyde and ethene (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of k(HO + benzaldehyde)/k(HO + ethene) = 1.6 ± 0.1 is placed on an absolute basis using k(HO + ethene) = 7.9×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (IUPAC, 2019).

(b) HO radicals were generated by the photolysis of HONO at λ = 300-450 nm in air at atmospheric pressure in a 220 L Tedlar chamber. The concentrations of benzaldehyde and ethene (the reference compound) were measured by GC-FID. The measured rate coefficient ratio of k(HO + benzaldehyde)/k(HO + ethene) = 1.39 ± 0.27 is placed on an absolute basis using k(HO + ethene) = 7.9×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K and atmospheric pressure (IUPAC, 2019).

(c) HO radicals were generated by the photolysis of CH_3ONO in air at atmospheric pressure in a ~200 L Tedlar chamber. Benzaldehyde and diethyl ether (the reference compound) were monitored by GC, and the measured rate coefficient ratio k(HO + benzaldehyde)/k(HO + diethyl ether) = $0.721 \exp[(89.5 \pm 84.7)/T]$ over the temperature range 294-343 K is placed on an absolute basis using a rate coefficient of k(HO + diethyl ether) = $1.15 \times 10^{-17}\ T^2 \exp(743/T)$ cm^3 molecule^{-1} s^{-1} (Calvert et al., 2009).

(d) HO radicals were generated by the photolysis of HONO at λ = 300-460 nm in air at atmospheric pressure in a 200 L Teflon chamber. The concentrations of benzaldehyde, di-isopropyl ether, diethyl ether and 1,3-dioxolane (the reference compounds) were measured by GC-FID. The measured rate coefficient ratios of k(HO + benzaldehyde)/k(HO + di-isopropyl ether) = 1.12 ± 0.04, k(HO + benzaldehyde)/k(HO + diethyl ether) = 0.97 ± 0.02 and k(HO + benzaldehyde)/k(HO + 1,3-dioxolane) = 1.15 ± 0.02 are placed on an absolute basis by using k(HO + di-isopropyl ether) = 1.0×10^{-11}, k(HO + diethyl ether) = 1.24 ×

10^{-11} and k(HO + 1,3-dioxolane) = 1.0 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K and atmospheric pressure (Calvert et al., 2009).

(e) HO radicals generated by the photolysis of CH_3ONO in air at atmospheric pressure in two different FEP Teflon chambers (350 L and 3910 L). The concentrations of benzaldehyde, di-n-butyl ether, tetrahydrofuran, 1,2,4-trimethylbenzene, diethyl ether and n-hexane (the reference compounds) were measured by GC-FID during the experiments. The measured rate coefficient ratios of k(HO + benzaldehyde)/k(HO + di-n-butyl ether) = 0.45 ± 0.04, k(HO + benzaldehyde)/k(HO + tetrahydrofuran) = 0.80 ± 0.02, k(HO + benzaldehyde)/k(HO + 1,2,4-trimethylbenzene) = 0.45 ± 0.06, k(HO + benzaldehyde)/k(HO + diethyl ether) = 1.05 ± 0.06 and k(HO + benzaldehyde)/k(HO + *n*-hexane) = 2.63 ± 0.12 are placed on an absolute basis using k(HO + di-n-butyl ether) = 2.9 × 10^{-11}, k(HO + tetrahydrofuran) = 1.7 × 10^{-11}, k(HO + diethyl ether) = 1.24 × 10^{-11} (Calvert et al., 2009), k(HO + *n*-hexane) = 5.48 × 10^{-12} (Calvert et al., 2008) and k(HO + 1,2,4-trimethylbenzene) = 3.25 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Calvert et al., 2002) at 298 K and atmospheric pressure and 295 K.

(f) Relative to HO + ethene
(g) Relative to HO + diethyl ether
(h) Relative to HO + di-isopropyl ether
(i) Relative to HO + 1,3-dioxolane
(j) Relative to HO + di-n-butyl ether
(k) Relative to HO + tetrahydrofuran
(l) Relative to 1,2,4-trimethylbenzene
(m) Relative to *n*-hexane

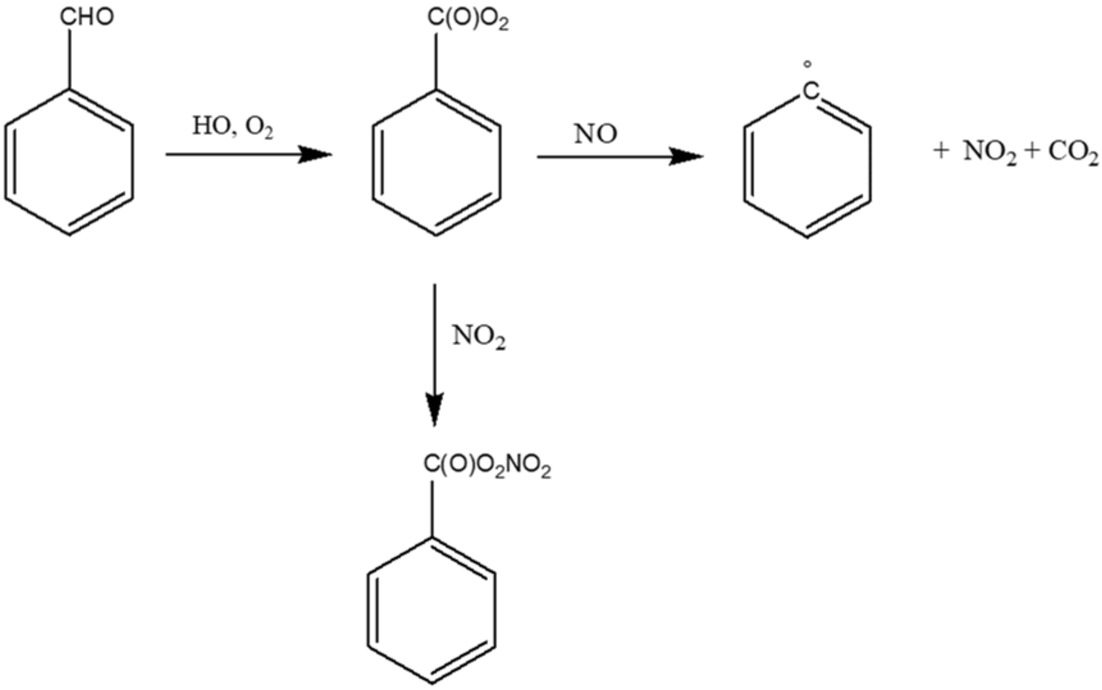
Preferred Values

Parameter	Value	*T*/K
k/ $molecule^{-1}$ s^{-1}	1.26 × 10^{-11}	298
k/ cm^3 $molecule^{-1}$ s^{-1}	5.9 × 10^{-12} exp(225/T)	290-350
Reliability		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 170	

Comments on Preferred Values

The rate coefficient values reported near 298 K by different authors are in agreement within the experimental uncertainties. The preferred value at 298 K is an average of these determinations. Semadeni et al. (1995) measured the temperature dependence using a relative method in the temperature range 289-373 K but used only the data in the range 294-343 K to derive their Arrhenius expression. The preferred temperature dependence values are obtained by combining the preferred k(298) value with the sole temperature dependence of Semadeni et al. in the restricted temperature range 294-343K.

Reaction of HO with benzaldehyde proceeds mainly by abstraction of the aldehydic H-atom to form benzoyl radical which adds O_2 to form benzoyl peroxy radical. In presence of NOx, benzoyl peroxy radical reacts with NO or NO_2:



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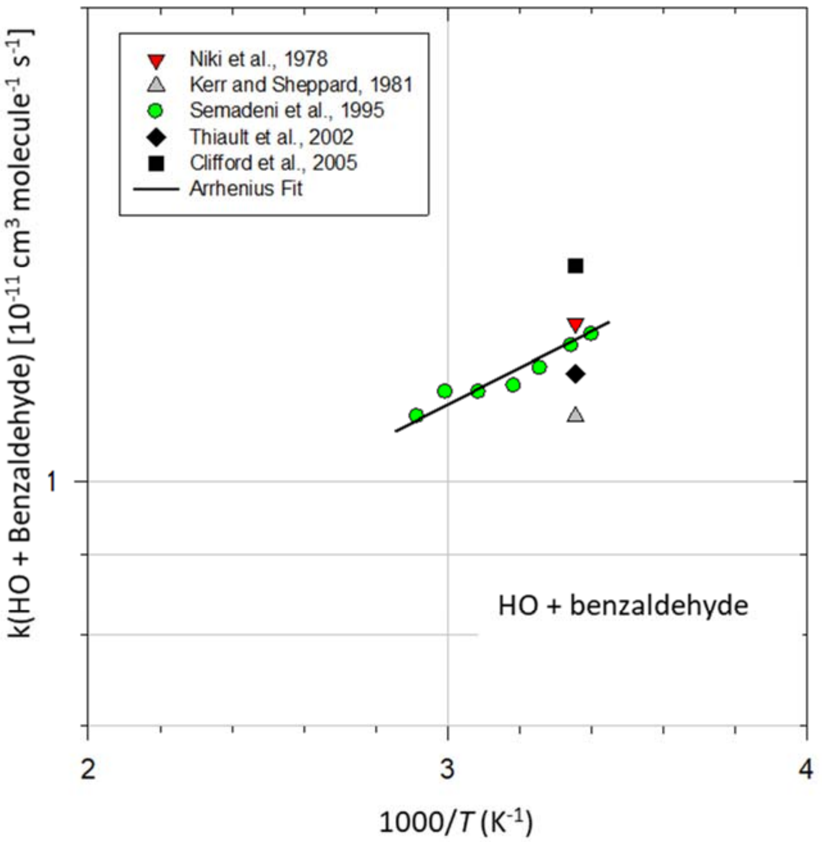

Rate coefficients for HO + benzaldehyde.

HOx_AROM26: benzyl alcohol

Last evaluated: June 2019; Last change in preferred values: June 2019

HO + $C_6H_5CH_2OH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.75 \pm 0.66) \times 10^{-11}$	297 ± 3	Harrison and Wells, 2009	RR-GC (a, b)
$(2.61 \pm 0.58) \times 10^{-11}$	297 ± 3	Harrison and Wells, 2009	RR-GC (a, c)
$(2.7 \pm 0.7) \times 10^{-11}$	298 ± 2	Bernard et al., 2013	RR-FTIR (e, f)
$(2.7 \pm 0.8) \times 10^{-11}$	298 ± 2	Bernard et al., 2013	RR-FTIR (e, g)
$(2.9 \pm 0.4) \times 10^{-11}$	296	Bernard et al., 2013	RR-FTIR (h)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures in 1 atmosphere of air at $\lambda > 300$ nm. Experiments were carried out in a ~50-80 liter Teflon chamber, and the concentrations of benzyl alcohol, n-decane and hexanal (the reference compounds) were measured during the experiments by gas chromatography. The measured rate coefficient ratios of k(HO + benzyl alcohol)/k(HO + n-decane) = 2.5 ± 0.6 and k(HO + benzyl alcohol)/k(HO + hexanal) = 0.9 ± 0.2 are placed on an absolute basis using k(HO + n-decane) = 1.1×10^{-11} cm^3 molecule^{-1} s^{-1} and k(HO + hexanal) = 2.9×10^{-11} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2008).

(b) Relative to HO + n-decane

(c) Relative to HO + hexanal

(e) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures in 1013 mbar of air at $\lambda > 300$ nm (centered at 365 nm). Experiments were carried out in a ~7300 liter Teflon chamber, and the concentrations of benzyl alcohol, di-n-butyl ether and propene (the reference compounds) were measured during the experiments by FTIR. The measured rate coefficient ratios of k(HO + benzyl alcohol)/k(HO + di-n-butyl ether) = 0.96 ± 0.12 and k(HO + benzyl alcohol)/k(HO + propene) = 0.93 ± 0.06 are placed on an absolute basis using k(HO + di-n-butyl ether) = 2.8×10^{-11} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2011) and k(HO + propene) = 2.9×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(f) Relative to HO + di-n-butyl ether

(g) Relative to HO + propene

(h) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures in 933 mbar of air at $\lambda > 300$ nm. Experiments were carried out in a ~140 liter Pyrex chamber, and the concentrations of benzyl alcohol and ethene (the reference compound) were measured during the experiments by FTIR. The measured rate coefficient ratio of k(HO + benzyl alcohol)/k(HO + ethene) = 3.65 ± 0.18 are placed on an absolute basis using k(HO + ethene) = 7.9×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.7×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.08	298

Comments on Preferred Values

The results from Harrison and Wells (2009) and from Bernard et al. (2013) are in excellent agreement. The preferred value is an average of these two studies. The preferred value is in good agreement with the unpublished absolute measurement of Nolting et al., $k = (2.29\pm0.25) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K, cited in Atkinson (1989). Hippler et al. (1991) reported $k = 8.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at high temperature (1180-1450 K). This value was derived from a fit to the experimental profiles of stable products in shock-heated benzyl iodide/HNO_3/Ar mixtures.

The reaction proceeds both by H-atom abstraction from the $–CH_2OH$ group and via addition to the aromatic ring. H-atom abstraction from te $–CH_2OH$ group leads to the formation of benzaldehyde. In their mechanistic study, Harrison and Wells (2009) and Bernard et al. (2013) reported formation yied of ≈ 25% for benzaldehyde which reflects H-atom abstraction from $–CH_2OH$ group. According to these authors, the addition of HO radicals accounts to the aromatic ring accounts for ≈ 75% of the total reaction and leads to numereous species such as polyoxygenated aromatics (o-hydroxybenzyl alcohol, o-dihydroxybenzene, …), formaldehyde, glyoxal and 4-oxo-pentenal as products of the reaction. Bernard et al. (2013) have reported formation yields of (22±2)% for o-hydroxybenzyl alcohol and (10±3)% for o-dihydroxybenzene.

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NO3_VOC26: 2-methylpropane

Last evaluated: March 2009; Last change in preferred values: March 2009

$NO_3 + (CH_3)_3CH \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.1 \pm 0.2) \times 10^{-16}$	298	Bagley et al., 1990	DF-A (a)
$(4.5 \pm 1.6) \times 10^{-16}$	348		
$(8.0 \pm 0.8) \times 10^{-16}$	373		
$(2.3 \pm 0.4) \times 10^{-15}$	423		
$(5.4 \pm 1.2) \times 10^{-15}$	473		
$(1.30 \pm 0.24) \times 10^{-14}$	523		
$\leq(6 \pm 1) \times 10^{-16}$	298	Boyd et al., 1991	SF-A (b)
Relative Rate Coefficients			
$(9.8 \pm 2.1) \times 10^{-17}$	296 ± 1	Atkinson et al., 1984	RR-GC (c)
$(1.18 \pm 0.25) \times 10^{-16}$	298 ± 2	Barnes et al., 1990	RR-GC (d)

Comments

(a) NO_3 radicals were generated by the reaction of F and HNO_3 in a discharge-flow system and monitored by optical absorption at 662 nm. The majority of experiments were conducted at a total pressure of 2.7 mbar (2 Torr).

(b) Stopped-flow technique with optical absorption of NO_3 radicals at 662 nm. Secondary reactions were expected to be significant, with a stoichiometry factor of ≥2. The cited upper limit to the rate coefficient includes a stoichiometry factor of 2.0.

(c) NO_3 radicals were produced by the thermal decomposition of N_2O_5, and the concentrations of 2-methylpropane and 2,3-dimethylbutane (the reference organic) were measured by GC at 987 mbar (740 Torr). A rate coefficient ratio of $k(NO_3 + \text{2-methylpropane})/k(NO_3 + \text{2,3-dimethylbutane}) = 0.24 \pm 0.05$ was obtained and is placed on an absolute basis using $k(NO_3 + \text{2,3-dimethylbutane}) = 4.08 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1991).

(d) NO_3 radicals were produced by the thermal decomposition of N_2O_5, and the concentrations of 2-methylpropane and ethene were measured by GC at 1 bar total pressure. A rate coefficient ratio of $k(NO_3 + \text{ethene})/k(NO_3 + \text{2-methylpropane}) = 1.78 \pm 0.37$ was obtained and is placed on an absolute basis using $k(NO_3 + \text{ethene}) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.1×10^{-16}	298
k /cm^3 molecule^{-1} s^{-1}	$3.0 \times 10^{-12} \exp(-3050/T)$	290-430
Reliability		
$\Delta \log k$	± 0.10	298
$\Delta E/R$	± 300	290-430

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients measured by Bagley et al. (1990) over the temperature range 298-423 K (at temperatures above 423 K the Arrhenius plot exhibits upward curvature). A least-squares analysis of the 298-423 K rate coefficients of Bagley et al. (1990) results in the preferred Arrhenius expression. The preferred room temperature rate coefficient is in excellent agreement with the relative rate coefficients of Atkinson et al. (1984) and Barnes et al. (1990). At room temperature and below the reaction proceeds almost totally by H-atom abstraction from the tertiary CH group (Bagley et al., 1990; Atkinson, 1991).

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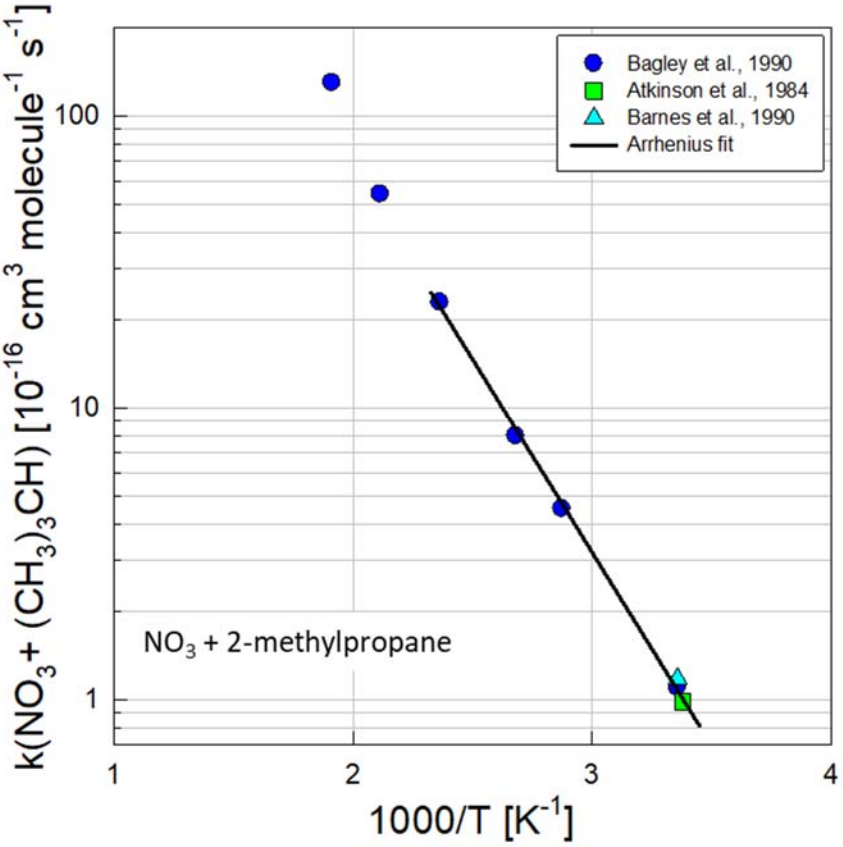

Rate coefficients for NO_3 + 2-methylpropane.

NO3_VOC27: 2-methylpropene

Last evaluated: March 2009; Last change in preferred values: March 2009

$NO_3 + (CH_3)_2C{=}CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(3.38 \pm 0.43) \times 10^{-13}$	298	Ravishankara and Mauldin, 1985	F-A (a)
$(3.4 \pm 0.7) \times 10^{-13}$	295 ± 2	Canosa-Mas et al., 1988	DF-A (b)
$(3.3 \pm 0.5) \times 10^{-13}$	298	Rahman et al., 1988	DF-MS (c)
$(3.87 \pm 0.42) \times 10^{-13}$	298	Benter et al., 1992	DF-MS (d)
$(3.6 \pm 0.4) \times 10^{-13}$	298	Wille et al., 1992	DF-MS (e)
Relative Rate Coefficients			
$(1.81 \pm 0.17) \times 10^{-13}$	300	Japar and Niki, 1975	RR-FTIR (f)
$(3.15 \pm 0.02) \times 10^{-13}$	298 ± 1	Atkinson et al., 1984	RR-GC (e)
$(3.35 \pm 0.51) \times 10^{-13}$	298 ± 2	Barnes et al., 1990	RR-GC (e)

Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5, and monitored by diode laser absorption at 662 nm.

(b) NO_3 radicals were generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3 in a flow system with uncoated Pyrex reactor in He gas at 2.7-6.7 mbar (2-5 Torr) and measured by optical absorption at 662 ± 2 nm. Rate coefficients derived from a second-order kinetic treatment of the experimental data with a 1:1 (NO_3:2-methylpropene) stoichiometry.

(c) NO_3 radicals were generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3 in a flow system in He gas. The experiments were conducted in excess of NO_3 over 2-methylpropene which was measured by MS.

(d) NO_3 radicals were generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3 in a flow system in He gas at 2.38 mbar. The experiments were conducted in excess of NO_3 over 2-methylpropene which was measured by MS.

(e) NO_3 radicals were generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3 in a flow system in He gas at 3 mbar. The experiments were conducted in excess of 2-methylpropene over NO_3 and the rate constant value determined from the oxirane product which was measured by MS.

(f) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The experiments were conducted in 1000 mbar (750 Torr) (200 mbar (150 Torr) of O_2 + 800 mbar (600 Torr) of Ar) at 300 K. The experimental data were relative to the equilibrium coefficient K for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm^3 molecule^{-1} at 300 K.

(g) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of 2-methylpropene and *trans*-2-butene (the reference compound) were measured by GC, and rate coefficient ratios of $k(NO_3 + \text{2-methylpropene})/k(NO_3 + \textit{trans}\text{-2-butene}) = 0.808 \pm 0.005$ (Atkinson et al., 1984) and 0.86 ± 0.13 (Barnes et al., 1990) obtained. These rate coefficient ratios are placed on an absolute basis using $k(NO_3$ + *trans*-2-butene) = 3.87×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 $molecule^{-1}$ s^{-1}	3.4×10^{-13}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Values

Rate coefficients are only available at room temperature, and the absolute and relative rate coefficients of Atkinson et al. (1984), Ravishankara and Mauldin (1985), Canosa-Mas et al. (1988), Rahmann et al., (1988), Barnes et al. (1990), Benter et al. (1992) and Wille et al. (1992) are in excellent agreement. The rate coefficient of Japar and Niki (1975) relative to the equilibrium constant for the $N_2O_5 \leftrightarrow NO_3 + NO_2$ reactions, which is subject to significant uncertainties, is a factor of ~2 lower than the other rate coefficients and is not used in the evaluation of the rate coefficient k. The preferred value is obtained from an average of the rate coefficients of Atkinson et al. (1984), Ravishankara and Mauldin (1985), Canosa-Mas et al. (1988), Rahmann et al., (1988), Barnes et al. (1990), Benter et al. (1992) and Wille et al. (1992). The NO_3 radical reaction with 2-methylpropene proceeds by initial addition,

$$NO_3 + (CH_3)_2C{=}CH_2 \rightarrow (CH_3)_2C^{\bullet}CH_2ONO_2^{*} \text{ or } (CH_3)_2C(ONO_2)C^{\bullet}H_2^{*}$$

with the chemically-activated nitrooxyalkyl radicals decomposing to oxirane + NO_2 in competition with collisional stabilization; for example

$$(CH_3)_2C^{\bullet}CH_2ONO_2^{*} \rightarrow \text{1,2-epoxy-2-methylpropane} + NO_2$$
$$(CH_3)_2C^{\bullet}CH_2ONO_2^{*} + M \rightarrow (CH_3)_2C^{\bullet}CH_2ONO_2 + M$$

Under atmospheric conditions the thermalized nitrooxybutyl radicals react with O_2 to form the corresponding peroxy radicals $(CH_3)_2C(OO^{\bullet})CH_2ONO_2$ and $(CH_3)_2C(ONO_2)CH_2OO^{\bullet}$. At atmospheric pressure of air, the observed products and their formation yields are: HCHO, 80% (Barnes et al., 1990) and 24 ± 8% (Hjorth et al., 1990); acetone, 85% (Barnes et al., 1990), 24 ± 8% (Hjorth et al., 1990), and 88% (Berndt and Böge, 1995); $(CH_3)_2CHCHO$, ~5% (Berndt and Böge, 1995); 1,2-epoxy-2-methylpropane, 7% (Berndt and Böge, 1995); and total nitrates, ~25% (Barnes et al., 1990). Some of the differences in reported yields are likely due to the experimental conditions and procedures used, with Barnes et al. (1990) and Berndt and Böge (1995) adding NO after the reaction to promote thermal decomposition of peroxynitrates and concurrently convert peroxy radicals to alkoxy radicals.

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NO3_VOC28: 1-butene

Last evaluated: March 2009; Last change in preferred values: March 2009

$NO_3 + CH_3CH_2CH{=}CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$2.5 \times 10^{-13} \exp[-(940 \pm 97)/T]$	299-473	Canosa-Mas et al., 1992	DF-A (a)
$(1.1 \pm 0.2) \times 10^{-14}$	299		
$5.2 \times 10^{-13} \exp[-(1067 \pm 31)/T]$	232-401	Rudich et al., 1996	F-A (b)
$(1.4 \pm 0.10) \times 10^{-14}$	298		
$(1.04 \pm 0.11) \times 10^{-14}$	298 ± 2	Berndt et al., 1998	F-LIF (b)
Relative Rate Coefficients			
$(1.29 \pm 0.14) \times 10^{-14}$	300	Japar and Niki, 1975	RR (c)
$(1.24 \pm 0.02) \times 10^{-14}$	298 ± 1	Atkinson et al., 1984	RR (d)
$(1.24 \pm 0.05) \times 10^{-14}$	296 ± 2	Atkinson et al., 1988	RR (e)
$(1.21 \pm 0.06) \times 10^{-14}$	296 ± 1	Andersson and Ljungström, 1989	RR (c)
$(1.27 \pm 0.19) \times 10^{-14}$	298 ± 2	Barnes et al., 1990	RR (d)
$(1.19 \pm 0.09) \times 10^{-14}$	298 ± 2	Chew et al., 1998	RR (d)
$(1.24 \pm 0.08) \times 10^{-14}$	296 ± 2	Aschmann et al., 2008	RR (e)

Comments

(a) NO_3 radicals generated by the thermal decomposition of N_2O_5.

(b) NO_3 radicals were generated by F + HNO_3 reaction in 2.7 mbar (2 Torr) total pressure of He and monitored by long path absorption at 662 nm; pseudo first order conditions.

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The experimental data were relative to the equilibrium coefficient *K* for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm^3 molecule^{-1} at 300 K and 3.53×10^{-11} cm^3 molecule^{-1} at 296 K ((IUPAC, 2019).

(d) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of 1-butene and propene (the reference compound) were measured by GC, and rate coefficient ratios of $k(NO_3 + \text{1-butene})/k(NO_3 + \text{propene}) = 1.304 \pm 0.012$ (Atkinson et al., 1984), 1.34 ± 0.20 (Barnes et al., 1990) and 1.25 ± 0.09 (Chew et al., 1998) obtained. These rate coefficient ratios are placed on an absolute basis using $k(NO_3 + \text{propene}) = 9.5 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

(e) NO_3 radicals were generated by the thermal decomposition of N_2O_5. The concentrations of 1-butene and thiophene (the reference compound) were measured by GC, and rate coefficient ratios of $k(NO_3 + \text{1-butene})/k(NO_3 + \text{thiophene}) = 0.315 \pm 0.011$ (Atkinson et al., 1988) and 0.316 ± 0.020 (Aschmann et al., 2008) obtained. These rate coefficient ratios are placed on an absolute basis using $k(NO_3 + \text{thiophene}) = 3.93 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1991).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.3×10^{-14}	298
k /cm^3 molecule^{-1} s^{-1}	$3.2 \times 10^{-13} \exp(-950/T)$	230-480
Reliability		
$\Delta \log k$	± 0.10	298
Δ E/R	± 200	230-480

Comments on Preferred Values

The available absolute and relative room temperature rate coefficients are in good agreement. The temperature dependencies measured by Canosa-Mas et al. (1992) and Rudich et al. (1996) are also in good agreement. The preferred values are derived from an un-weighted least-squares analysis of the absolute and relative rate coefficients of Atkinson et al. (1984, 1988), Barnes et al. (1990), Canosa-Mas et al. (1992), Rudich et al. (1996), Berndt et al. (1998), Chew et al. (1998) and Aschmann et al. (2008). Because of uncertainties in the equilibrium constant for the $N_2O_5 \leftrightarrow NO_3 + NO_2$ reactions, the data of Japar and Niki (1975) and Andersson and Ljungström (1989) are not used in the evaluation of the preferred values, although they are in agreement with the preferred value.

The NO_3 radical reaction with 1-butene proceeds by initial addition,

$NO_3 + CH_3CH_2CH{=}CH_2 \rightarrow CH_3CH_2C^{\bullet}HCH_2ONO_2^{*}$ or $CH_3CH_2CH(ONO_2)C^{\bullet}H_2^{*}$

with the chemically-activated nitrooxyalkyl radicals decomposing to 1,2-epoxybutane + NO_2 in competition with collisional stabilization; for example

$CH_3CH_2C^{\bullet}HCH_2ONO_2^{*} \rightarrow$ 1,2-epoxybutane + NO_2
$CH_3CH_2C^{\bullet}HCH_2ONO_2^{*} + M \rightarrow CH_3CH_2C^{\bullet}HCH_2ONO_2 + M$

Under atmospheric conditions the thermalized nitrooxybutyl radicals react with O_2 to form the corresponding 1,2-nitrooxybutylperoxy radicals $CH_3CH_2CH(OO^{\bullet})CH_2ONO_2$ and $CH_3CH_2CH(ONO_2)CH_2OO^{\bullet}$. At atmospheric pressure of air, Barnes et al. (1990) observed HCHO, propanal, and total nitrates with yields (per reacted molecule of $CH_3CH_2CH{=}CH_2$) of 11%, 12% and ~60%, respectively. Berndt and Böge (1995) observed formation of 1,2-epoxybutane, propanal and $CH_3CH_2C(O)CH_2ONO_2$, with yields of 18%, 65% and ~17%, respectively, the yields in this case defined as ([product]/Σ[product]).

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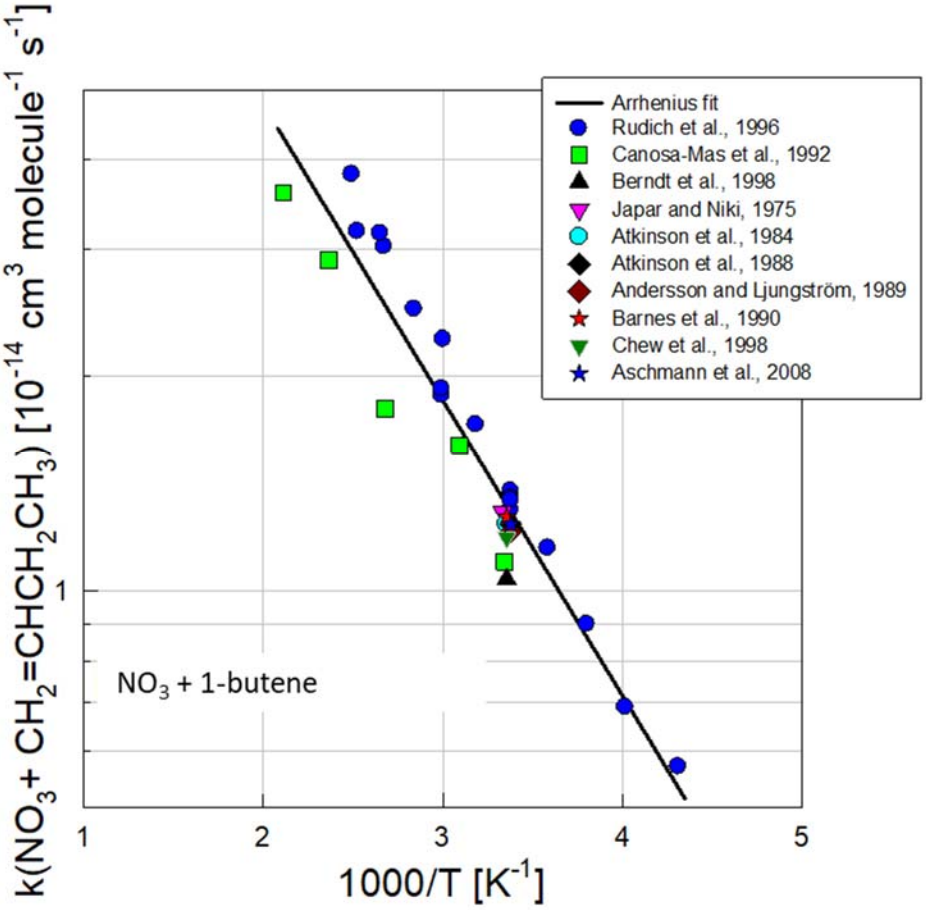

Rate coefficients for NO_3 + 1-butene

NO3_VOC29: *cis*-2-butene

Last evaluated: March 2009; Last change in preferred values: March 2009

NO_3 + *cis*-$CH_3CH{=}CHCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.75 \pm 0.24) \times 10^{-13}$	298	Benter et al., 1992	DF-MS (a)
$(3.3 \pm 0.8) \times 10^{-13}$	298	Wille et al., 1992	DF-MS (a)
Relative Rate Coefficients			
$(2.97 \pm 0.33) \times 10^{-13}$	300	Japar and Niki, 1975	RR-FTIR (b)
$(3.50 \pm 0.01) \times 10^{-13}$	298 ± 1	Atkinson et al., 1984	RR-GC (c)

Comments

(a) NO_3 radicals were generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3 in He carrier and monitored by MS.

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The experimental data were relative to the equilibrium coefficient K for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm^3 molecule^{-1} at 300 K.

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of *cis*-2-butene and *trans*-2-butene (the reference compound) were measured by GC, and rate coefficient ratios of k(NO_3 + *cis*-2-butene)/k(NO_3 + *trans*-2-butene) = 0.897 ± 0.003 (Atkinson et al., 1984) obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of k(NO_3 + *trans*-2-butene) = 3.9×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.5×10^{-13}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Values

Rate coefficients are only available at room temperature, and the absolute and relative rate coefficients of Atkinson et al. (1984), Benter et al. (1992) and Wille et al. (1992) are in good agreement. While the rate coefficient of Japar and Niki (1975) is in good agreement with those of Atkinson et al. (1984), Benter et al. (1992) and Wille et al. (1992), it is not used in the rate coefficient evaluation because of uncertainties in the equilibrium constant for the $N_2O_5 \leftrightarrow NO_3 + NO_2$ reactions. The preferred value is obtained from an average of the rate coefficients of Atkinson et al. (1984), Benter et al. (1992) and Wille et al. (1992).

The NO_3 radical reaction with *cis*-2-butene proceeds by initial addition,

NO_3 + *cis*-$CH_3CH{=}CHCH_3 \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3^*$

with the chemically-activated nitrooxyalkyl radicals decomposing to *cis*- or *trans*-2,3-epoxybutane + NO_2 in competition with collisional stabilization.

$CH_3C^{\bullet}HCH(ONO_2)CH_3^* \rightarrow$ 2,3-epoxybutane + NO_2
$CH_3C^{\bullet}HCH(ONO_2)CH_3^* + M \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3 + M$

Under atmospheric conditions the thermalized nitrooxybutyl radical reacts with O_2 to form the peroxy radical $CH_3CH(OO^{\bullet})CH(ONO_2)CH_3$. At atmospheric pressure of air, the observed products and their molar formation yields are: CH_3CHO, 34 ± 12% (Hjorth et al., 1990); $CH_3C(O)CH(ONO_2)CH_3$, 41 ± 13% (Hjorth et al., 1990); $CH_3CH(OH)CH(ONO_2)CH_3$, 15 ± 5% (Hjorth et al., 1990); and 2,3-epoxybutane, ≤1% (Skov et al., 1994).

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NO3_VOC30: *trans*-2-butene

Last evaluated: March 2009; Last change in preferred values: March 2009

NO_3 + *trans*-$CH_3CH{=}CHCH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(3.78 \pm 0.41) \times 10^{-13}$	298	Raviskankara and Mauldin, 1985	F-A/LIF (a)
$(1.78 \times 10^{-12} \exp[-(530 \pm 100)/T]) + (1.28 \times 10^{-14} \exp[(570 \pm 110)/T])$	204-378	Dlugokencky and Howard, 1989	F-LIF (b)
$(3.96 \pm 0.48) \times 10^{-13}$	298		
$(3.88 \pm 0.30) \times 10^{-13}$	298	Benter et al., 1992	DF-MS (c)
$(3.55 \pm 0.33) \times 10^{-13}$	267	Rudich et al., 1996	F-A (d)
$(4.06 \pm 0.36) \times 10^{-13}$	298		
$(3.74 \pm 0.45) \times 10^{-13}$	298 ± 2	Berndt et al., 1998	F-LIF (e)
$(3.78 \pm 0.17) \times 10^{-13}$	298 ± 2	Kasyutich et al., 2002	DF-A (f)
Relative Rate Coefficients			
$(2.31 \pm 0.17) \times 10^{-13}$	300	Japar and Niki, 1975	RR-FTIR (g)
$(3.09 \pm 0.27) \times 10^{-13}$	298 ± 1	Atkinson et al., 1984	RR-GC (g)

Comments

(a) NO_3 radicals generated by the thermal decomposition of N_2O_5 and were monitored by LIF at 662 nm, or were generated by the reaction F + HNO_3 and were monitored by long-path absorption at 662 nm at 0.53-1.47 mbar (0.4-1.1 Torr).

(b) NO_3 radicals were generated by the thermal decomposition of N_2O_5 at ~400 K and monitored by LIF. Experiments were carried out in a low-pressure flow tube at ~1.3-1.4 mbar (1.0-1.1 Torr) of He.

(c) NO_3 radicals were generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3 in He carrier gas and monitored by MS.

(d) NO_3 radicals were generated by the thermal decomposition of N_2O_5 at 400 K in a flow system, and NO_3 radical concentrations were measured by visible tunable diode laser absorption at 661.9 nm at 2-4 mbar (1.5-3 Torr) of He.

(e) NO_3 radicals were generated by the thermal decomposition of N_2O_5 at ~400 K and monitored by LIF. Experiments were carried out in a low-pressure flow tube at ~ 3 mbar (2.5 Torr) of He.

(f) NO_3 radicals were generated by the reaction F + HNO_3 and were monitored by off-axis cavity-enhanced laser absorption spectroscopy at 662 nm.

(g) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The experimental data were relative to the equilibrium coefficient *K* for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm^3 molecule^{-1} at 300 K and 2.75×10^{-11} cm^3 molecule^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.9×10^{-13}	298
k /cm^3 molecule^{-1} s^{-1}	$\{1.78 \times 10^{-12} \exp(-530/T) + 1.28 \times 10^{-14} \exp(570/T)\}$	200-380
Reliability		
$\Delta \log k$	± 0.08	200-380

Comments on Preferred Values

The available absolute 298 K rate coefficients are in excellent agreement, as are those of Dluokencky and Howard (1989) and Rudich et al. (1996) at 267 K. Because of uncertainties in the equilibrium constant for the $N_2O_5 \leftrightarrow NO_3 + NO_2$ reactions, the data of Japar and Niki (1975) and Atkinson et al. (1984) are not used in the evaluation of the preferred values. The temperature-dependent rate expression of Dlugokencky and Howard (1989) is accepted as the preferred value. There is no evidence for a pressure dependence of the room temperature rate constant over the pressure range 0.4-740 Torr as reported by the available studies.

The NO_3 radical reaction with *trans*-2-butene proceeds by initial addition,

NO_3 + *cis*-$CH_3CH{=}CHCH_3 \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3^*$

with the chemically-activated nitrooxyalkyl radicals decomposing to *cis*- or *trans*-2,3-epoxybutane + NO_2 in competition with collisional stabilization.

$CH_3C^{\bullet}HCH(ONO_2)CH_3^* \rightarrow$ 2,3-epoxybutane + NO_2
$CH_3C^{\bullet}HCH(ONO_2)CH_3^* + M \rightarrow CH_3C^{\bullet}HCH(ONO_2)CH_3 + M$

Under atmospheric conditions the thermalized nitrooxybutyl radical reacts with O_2 to form the peroxy radical $CH_3CH(OO^{\bullet})CH(ONO_2)CH_3$. At atmospheric pressure of air, the observed products and their molar formation yields are: CH_3CHO, 70% (Barnes et al., 1990), 34 ± 12% (Hjorth et al., 1990) and ~100% (Berndt and Böge, 1995); $CH_3C(O)CH(ONO_2)CH_3$, 55% (Barnes et al., 1990), 41 ± 13% (Hjorth et al., 1990) and 38% (Berndt and Böge, 1995); $CH_3CH(OH)CH(ONO_2)CH_3$, 15 ± 5% (Hjorth et al., 1990); $CH_3CH(ONO_2)CH(ONO_2)CH_3$, 4% (Barnes et al., 1990); and 2,3-epoxybutane, ≤1% (Skov et al., 1994) and 12% (Berndt and Böge, 1995). Some of these differences in reported yields are likely due to the experimental conditions and procedures used, with Barnes et al. (1990) and Berndt and Böge (1995) adding NO after the reaction to promote thermal decomposition of peroxynitrates and concurrently convert peroxy radicals to alkoxy radicals.

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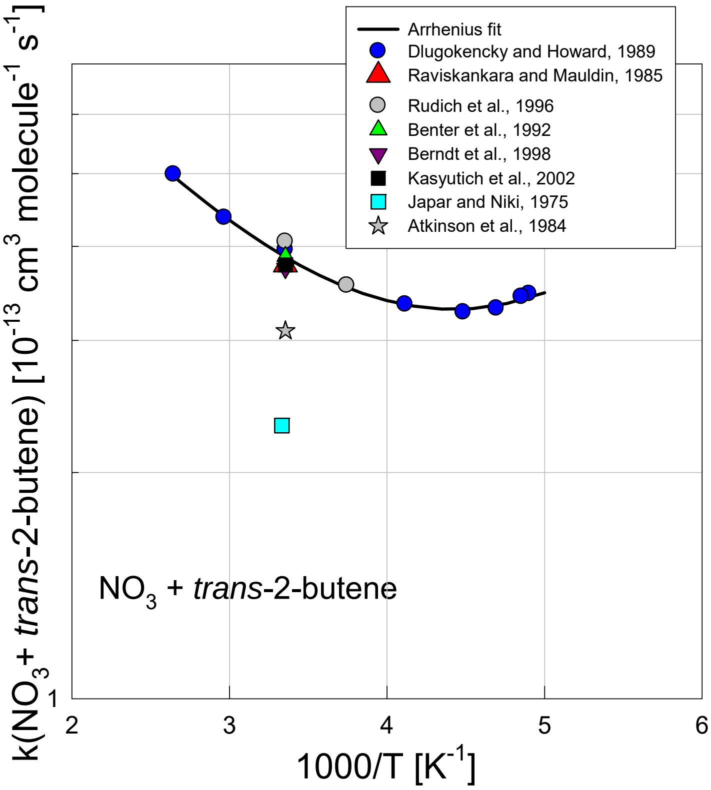
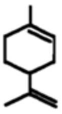


Rate coefficients for NO_3 + *trans*-2-butene

NO3_VOC33: *d*-limonene

Last evaluated: June 2013; Last change in preferred values: June 2015

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(9.4 \pm 0.9) \times 10^{-12}$	298	Martínez et al., 1999	DF-LIF (a)
$(5.8 \pm 0.7) \times 10^{-12}$	433		
Relative Rate Coefficients			
$(1.31 \pm 0.04) \times 10^{-11}$	295	Atkinson et al., 1984	RR (b)
$(1.12 \pm 0.17) \times 10^{-11}$	298	Barnes et al., 1990	RR (c)

Limonene is 4-isopropenyl-1-methyl-cyclohexene.

Comments

(a) NO_3 radicals (6-30 × 10^{11} molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He. Limonene was present at similar concentrations (1-3 fold) to NO_3, so that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Limonene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3 + \text{limonene}) / k(NO_3 + \text{2-methyl-2-butene}) = 1.40 \pm 0.04$ is placed on an absolute basis by $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(c) 420 L glass chamber at 298 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Limonene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3 + \text{limonene}) / k(NO_3 + \text{2-methyl-2-butene}) = 1.20 \pm 0.18$ is placed on an absolute basis by $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.2×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate studies, which indicate a larger rate coefficient than observed in the single absolute study.

The difference between the rate coefficients obtained at 298 and 433 K (factor 1.6) was not considered large enough to warrant a more detailed investigation of the temperature dependence (Martínez et al., 1999).

The reaction mechanism involves the initial addition of NO_3 across a double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Product studies suggest that attack of NO_3 at the exocyclic double bond of limonene is insignificant (Spittler et al 2006), which is supported by theoretical calculations (Jiang et al., 2009).

The reaction products in air include endolim (yield of 29 %, Spittler et al., 2006) and organic nitrates (expected to include both mono- and dinitrates) with yields (per limonene reacted) between 30 and 67 % (Spittler et al. 2006; Hallquist et al., 1999; Fry et al 2011; Fry et al., 2014). Using thermal dissociation of alkyl nitrates and peroxynitrates coupled to LIF detection of NO_2, Fry et al., (2014) derived a molar organic nitrate yield (gas- and aerosol) of 0.54 with 83 % being located in the aerosol phase. Organonitrates comprised 82 % of the aerosol mass.

Secondary organic aerosol is formed efficiently in smog-chamber studies of the reaction between NO_3 and limonene with mass-based yields of between 17 and 57% reported (Hallquist et al., 1999; Fry et al., 2011; Fry et al., 2014). Spittler et al. (2006) suggest that much of the organic aerosol is formed from further reactions of endolim.

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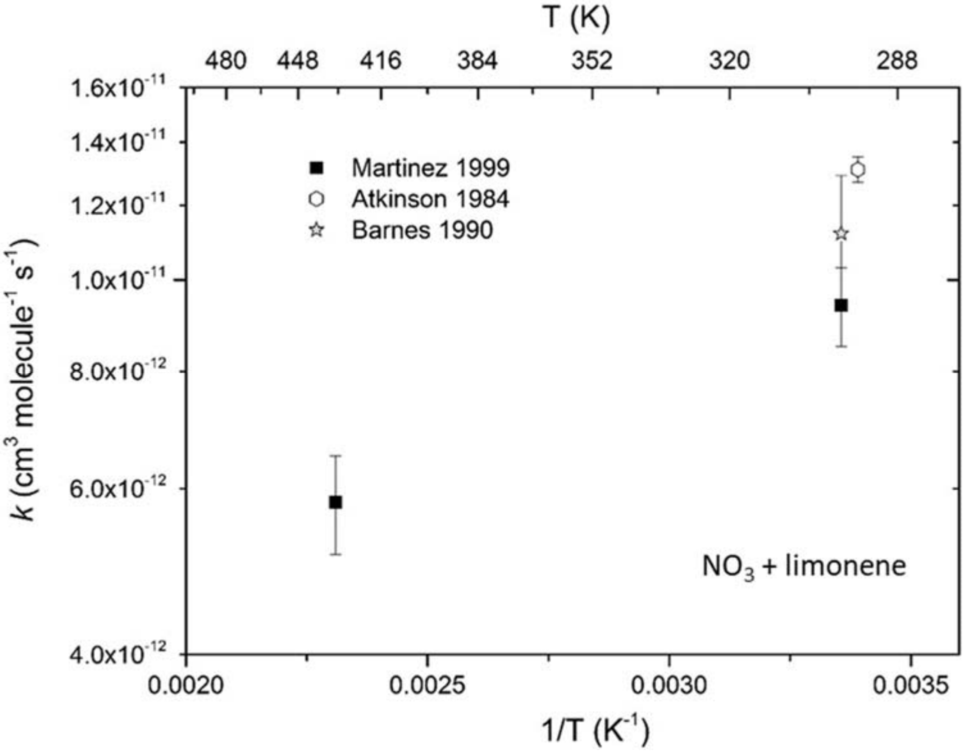
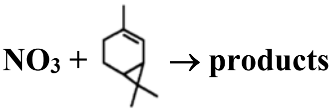


Rate coefficients for NO_3 + limonene

NO3_VOC34: 2-carene

Last evaluated: June 2013; Last change in preferred values: June 2013



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.66 \pm 0.18) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$1.4 \times 10^{-12} \exp[(741\pm 190)/T]$	298-433		
Relative Rate Coefficients			
$(1.87 \pm 0.11) \times 10^{-11}$	295	Corchnoy and Atkinson, 1990	RR-GC (b)
$(2.16 \pm 0.36) \times 10^{-11}$	295	Corchnoy and Atkinson, 1990	RR-GC (c)

2-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-2-ene.

Comments

(a) NO_3 radicals ($6\text{-}30 \times 10^{11}$ molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He at 4 temperatures between 298 and 433 K. 2-carene was present at similar concentrations (1-3 fold) to NO_3, so that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. 2-carene and 2-methyl-2-butene (reference reactant) were monitored by GC to obtain the rate constant ratio $k(NO_3 + \text{2-carene}) / k(NO_3 + \text{2-methyl-2-butene}) = 2.00 \pm 0.12$. Using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003) the absolute rate constants listed in the table is obtained.

(c) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. 2-carene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC to obtain the rate constant ratio $k(NO_3 + \text{2-carene}) / k(NO_3 + \text{2,3-dimethyl-2-butene}) = 0.377 \pm 0.063$. Using $k(NO_3 + \text{2,3-dimethyl-2-butene}) = 5.72 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) the absolute rate constant listed in the table is obtained.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.0×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The three determinations of the room temperature rate coefficient agree to within ~30 % and the preferred value of the room temperature rate coefficient is based on the relative rate studies. The temperature dependence observed by Martínez et al. (1999) requires validation before a recommendation can be made.

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical or decompose to release NO_2. At atmospheric pressure the formation of the peroxy radical will generally dominate.

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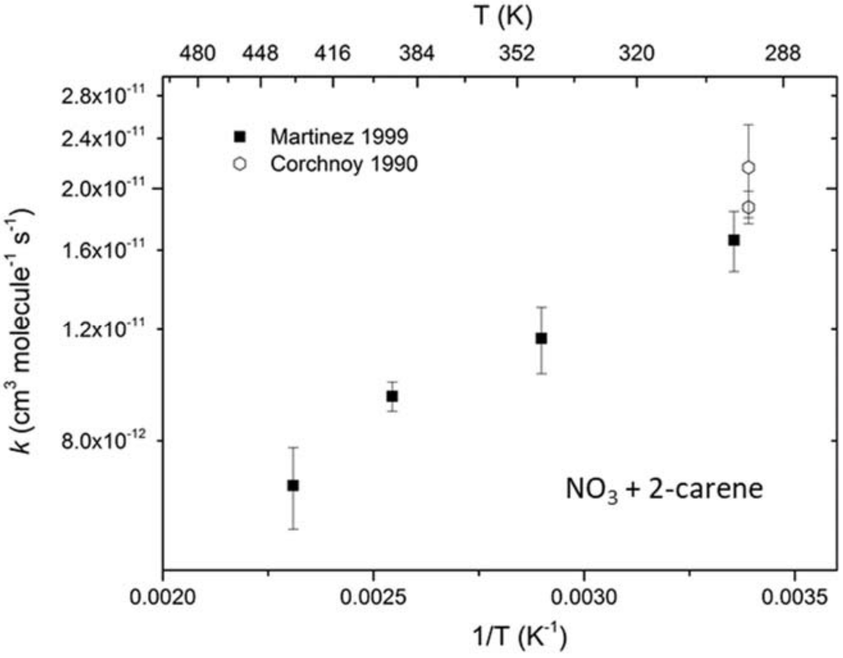
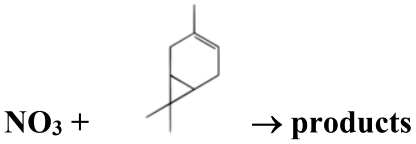


Rate coefficients for NO_3 + 2-carene.

NO3_VOC35: 3-carene

Last evaluated: June 2013; Last change in preferred values: June 2013



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.01 \pm 0.02) \times 10^{-11}$	295	Atkinson et al., 1984	RR (a)
$(8.2 \pm 1.2) \times 10^{-12}$	298	Barnes et al., 1990	RR (b)

3-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-3-ene.

Comments

(a) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. 3-carene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3 + \text{3-carene}) / k(NO_3 + \text{2-methyl-2-butene}) = 1.08 \pm 0.02$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(b) 420 L glass chamber at 298 K and 1 bar of air. NO_3 was generated by the thermal decomposition of N_2O_5. 3-carene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3 + \text{3-carene}) / k(NO_3 + \text{2-methyl-2-butene}) = 0.87 \pm 0.13$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	9.1×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The two relative rate studies of this reaction are at room temperature only. Both Atkinson et al. (1984) and Barnes et al. (1990) used the same reference reactant but derived rate coefficients which diverge by ~20 %. There is no obvious reason to favour either study and the preferred value of the 298 K rate coefficient is an unweighted average.

The reaction mechanism involves the addition of NO_3 across the double bond to form a nitrooxyalkyl radical, which, in air, forms a nitrooxyalkyl peroxy radical. Unstable nitrooxy peroxynitrates (from nitrooxyalkyl peroxy radical + NO_2) were observed at early reaction times

(Hallquist et al. 1999). These authors also identified the end products caronaldehyde (molar yields of 2-3 %), carbonyls (estimated molar yield of 20-30 %) and nitrates (66-74 %). The atmospheric fate of caronaldehyde is expected to be reaction with OH and photolysis (Hallquist et al., 1997).

Using thermal dissociation of alkyl nitrates and peroxynitrates coupled to LIF detection of NO_2, Fry et al., (2014) derived a molar organic nitrate yield (gas- and aerosol) of 0.77 with 50 % being located in the aerosol phase. Organonitrates comprised 56 % of the aerosol mass.

Secondary organic aerosol has been observed in the smog-chamber studies of NO_3 + 3-carene (Hallquist et al., 1999; Griffin et al. 1999) with mass-based yields of up to 72 % depending on the amount of 3-carene reacted. Hallquist et al. provide evidence for the presence of condensable organics containing the $-ONO_2$ entity. A detailed mechanism of the potential routes to aerosol formation is presented by Colville et al. (2004).

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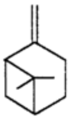
NO3_VOC36: β-pinene

Last evaluated: June 2013; Last change in preferred values: June 2013

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.36 \pm 0.10) \times 10^{-12}$	295	Atkinson et al., 1984	RR-GC (a)
$(2.38 \pm 0.05) \times 10^{-12}$	296	Atkinson et al., 1988	RR-GC (b)
$(1.1 \pm 0.4) \times 10^{-12}$	298*	Kotzias et al., 1989	RR-FTIR (c)
$(2.81 \pm 0.47) \times 10^{-12}$	298	Barnes et al., 1990	RR-GC (d)

β-pinene is 6,6-dimethyl-2-methylene-bicyclo[3.1.1]heptane.
*) the experimental temperature was "room temperature" which we list as 298K.

Comments

(a) 6400 L Teflon chamber at 295 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. β-pinene and 2-methyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio, k(NO_3 + β-pinene) / k(NO_3 + 2-methyl-2-butene) = 0.252 ± 0.011 is placed on an absolute basis using k(NO_3 + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(b) 6400 L Teflon chamber at 296 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. β-pinene and *trans*-2-butene (reference reactant) were monitored by GC. The rate constant ratio, k(NO_3 + β-pinene) / k(NO_3 + *trans*-2-butene) = 6.10 ± 0.14 is placed on an absolute basis using k(NO_3 + *trans*-2-butene) = 3.9×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

(c) 450 L Teflon-coated glass reactor, with β-pinene, N_2O_5 and NO_2 monitored by FTIR. NO_3, NO_2 and N_2O_5 were assumed to be in equilibrium and the NO_3 concentration was calculated from the equilibrium constant (1.9×10^{-11} molecule^{-1} cm^3) and used to derive the rate constant from the β-pinene decay constant. The authors did not quote the temperature of these experiments, making re-assessment of their data via e.g. use of a more recently measured equilibrium constant difficult.

(d) 420 L glass chamber at 298 K and 1 bar of air. NO_3 was generated by the thermal decomposition of N_2O_5. β-pinene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, k(NO_3 + β-pinene) / k(NO_3 + 2-methyl-2-butene) = 0.30 ± 0.05 is placed on an absolute basis using k(NO_3 + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.5×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The relative rate studies of this reaction which employed either 2-methyl-2-butene or *trans*-2-butene as reference reactants are in broad agreement, though there is no obvious reason why Atkinson et al. (1984) and Barnes et al. (1990), who used the same reference reactant should derive rate coefficients which diverge by ~20 %. These studies are preferred over that of Kotzias et al. (1989), as there are greater uncertainties related to using the strongly temperature dependent equilibrium constant for the $NO_2 + NO_3 \rightleftharpoons N_2O_5$ reaction, which are compounded by the fact that authors did not cite their experimental temperature. The preferred value of the 298 K rate coefficient is thus an unweighted average of the results derived by Atkinson et al. (1984, 1988) and Barnes et al. (1990).

The reaction mechanism involves the addition of NO_3 across the double bond to form a nitrooxyalky radical, which, in air, forms a nitrooxyalkyl peroxy radical. Hallquist et al. (1999) identified the end products nopinone (molar yields of 1-2 %), carbonyls (estimated molar yield of 12-14 %) and organic nitrates (estimated molar yield of 61-74 %) which were also observed using FTIR and MS by Kotzias et al. (1989), but not quantified. Using thermal dissociation of alkyl nitrates and peroxynitrates coupled to LIF detection of NO_2, Fry et al., (2009) derived a molar organic nitrate yield of ~40 %. Hydroxynitrates (m/z = 215), hydroxycarbonyl nitrazes (m/z = 229) and dihydroxynitrates / hydroperoxides and cyclic ether hydroxynitrates (m/z = 231) have been observed as gas-phase products (Boyd et al., 2015), with altogether more than forty C_7-C_{10} organic nitrates (in both gas and particle phase) possessing between 4 and 9 oxygen atoms detected (Boyd et al. 2015, Nah et al., 2016). Formation of peroxy radical that may perform intramolecular H-abstraction (auto-oxidation) has been proposed as a potential explanation for the high O-to-N ratios observed.

Secondary organic aerosol formation has been observed in the smog-chamber studies of NO_3 + β-pinene (Hallquist et al., 1999; Griffin et al. 1999; Fry et al., 2009, 2014: Boyd et al., 2015; Nah et al., 2016) with mass-based yields of up to 100 % depending on the amount of β-pinene reacted. The aerosol yield is not strongly influenced by relative humidity, seed-aerosol acidity or whether the fate of RO_2 is reaction with NO_3 or HO_2 (Boyd et al., 2015).

Organonitrates were found to comprise ≈ 45-75 % of the aerosol mass (Fry et al., 2014, Boyd et al., 2015: Nah et al., 2016) with evidence for particle-phase hydrolysis of tertiary nitrates (Boyd et al., 2015).

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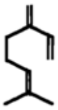
NO3_VOC37: myrcene

Last evaluated: June 2013; Last change in preferred values: June 2013

NO_3 +  → **products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.28 \pm 0.11) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$2.2 \times 10^{-12} \exp[(523 \pm 35)/T]$	298-433		
Relative Rate Coefficients			
$(1.06 \pm 0.02) \times 10^{-11}$	294	Atkinson et al., 1985	RR (b)

Myrcene is 7-methyl-3-methylene-1,6-octadiene.

Comments

(a) NO_3 radicals ($6\text{-}30 \times 10^{11}$ molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He. Myrcene was present at similar concentrations (1-3 fold) to NO_3, so that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 4000 L Teflon chamber at 294 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Correction made to the myrcene loss rate due to reaction with NO_2 was < 18 %. Myrcene and 2-methyl-2-butene were monitored by GC. The rate constant ratio, $k(NO_3 + \text{myrcene}) / k(NO_3 + \text{2-methyl-2-butene}) = 1.13 \pm 0.02$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.1×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1985) in which absolute determination of the reactant concentrations was not required. The error limits are expanded to reflect the necessity to correct for removal of myrcene by reaction with NO_2 and the ≈ 20 % difference to the absolute rate measurement (Martínez et al., 1999). The temperature dependence observed by Martínez et al. (1999) requires validation before a recommendation can be made.

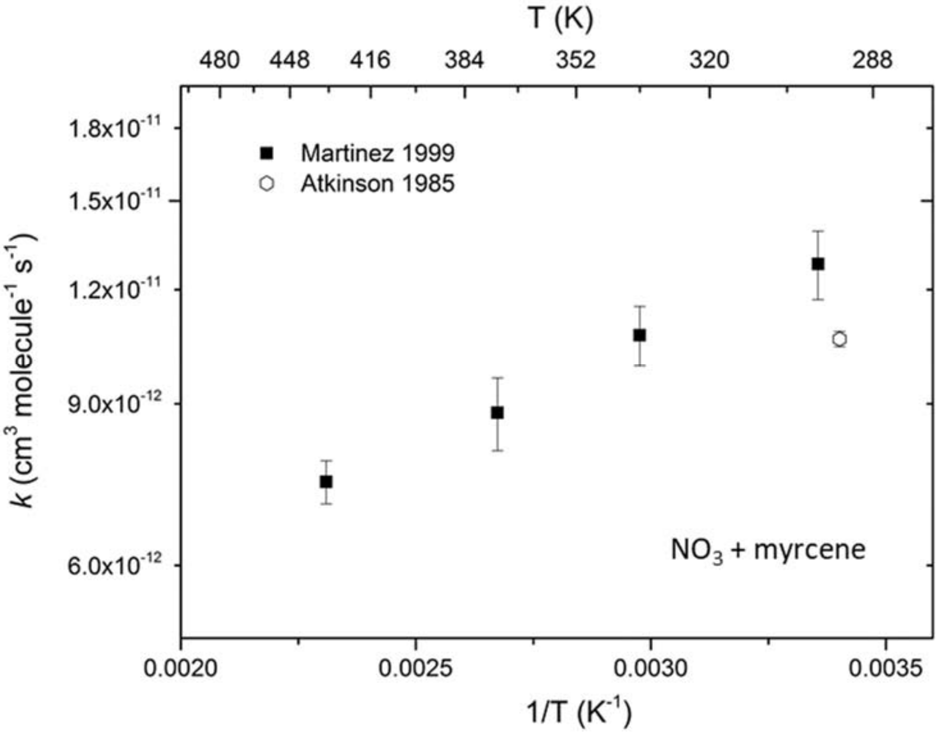
There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical or decompose to release NO_2. At atmospheric pressure the formation of the peroxy radical will generally dominate.

References

Atkinson, R., Aschmann, S. M., Winer, A. M. and Pitts, J. N.: Env. Sci. Tech., 19, 159-163, 1985.

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.

Martínez, E., Cabañas, B., Aranda, A., Martín, P. and Salgado, S.: J. Atmos. Chem., 33, 265-282, 1999.



Rate coefficient for NO_3 + myrcene.

NO3_VOC38: sabinene

Last evaluated: June 2013; Last change in preferred values: June 2013

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(1.07 \pm 0.16) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$2.3 \times 10^{-10} \exp[-(940 \pm 200)/T]$	298-393		
Relative Rate Coefficients			
$(1.01 \pm 0.03) \times 10^{-11}$	296	Atkinson et al., 1990	RR (b)

Sabinene is 1-isopropyl-4-methylene-bicyclo[3.1.0]hexane.

Comments

(a) NO_3 radicals ($6\text{-}30 \times 10^{11}$ molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He at 4 temperatures between 298 and 393 K. Sabinene was present at similar concentrations (1-3 fold) to NO_3, so that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) Relative rate of loss of sabinene and 2-methyl-2-butene (reference reactant) in a 6400 L Teflon chamber at 980 mbar (735 Torr) of air was monitored by GC. NO_3 was generated by the thermal decomposition of N_2O_5. The rate constant ratio, $k(NO_3 + \text{sabinene}) / k(NO_3 + \text{2-methyl-2-butene}) = 1.08 \pm 0.03$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.10	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Atkinson et al. (1990). The significant, positive dependence of k on temperature observed by Martínez et al. (1999) requires validation.

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitro-oxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical.

Secondary organic aerosol has been observed in the smog-chamber studies of NO_3 + sabinene (Fry et al., 2014) with mass-based yields of up to 45 % (at 10 μg m^{-3} aerosol loading).

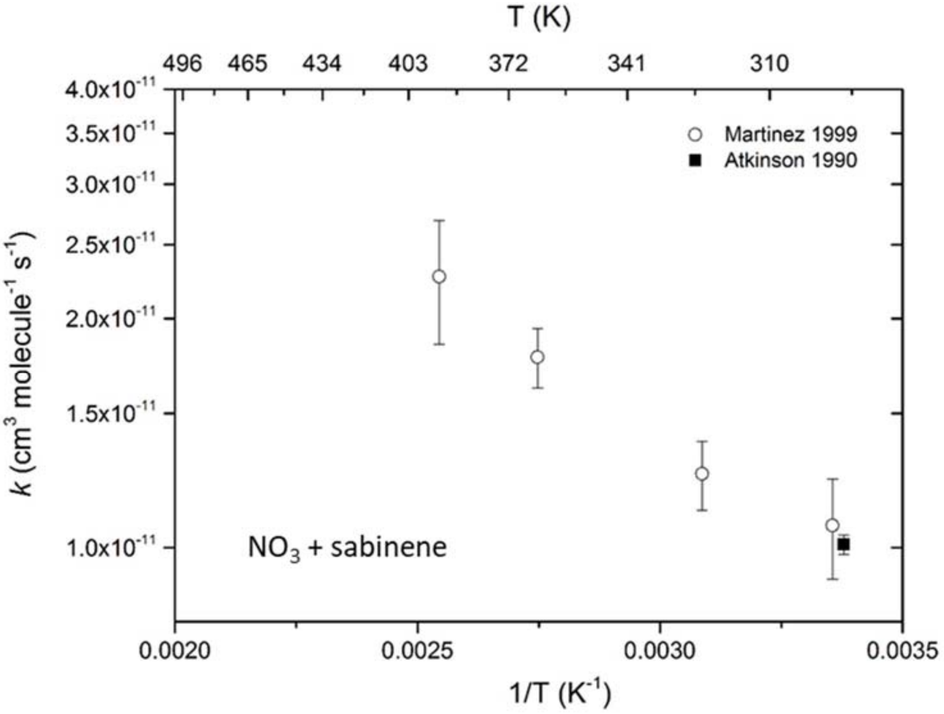
References

Atkinson, R., Aschmann, S. M. and Arey, J., Atmos. Env., A, 24, 2647-2654, 1990.

Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C. and Lee, L., Env. Sci. Tech., 48, 11944-11953, 2014.

Martínez, E., Cabañas, B., Aranda, A., Martín, P. and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.

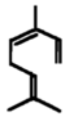


Rate coefficients for NO_3 + sabinene.

NO3_VOC39: *cis-/trans*-ocimene

Last evaluated: June 2013; Last change in preferred values: June 2013

NO_3 +



→ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(2.23 \pm 0.06) \times 10^{-11}$	294	Atkinson et al., 1985	RR (a)

Ocimene is 3,7-dimethyl-1,3,6-octatriene.

Comments

(a) 4000 L Teflon chamber at 294 K and 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Ocimene and 2-methyl-2-butene were monitored by GC. Correction made to the ocimene loss rate due to reaction with NO_2 was < 12 %. The rate constant ratio, $k(NO_3 + \text{ocimene}) / k(NO_3 + \text{2-methyl-2-butene}) = 2.38 \pm 0.06$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003). The rate constants for the cis and *trans*-isomers of ocimene were indistinguishable within experimental uncertainty (8%).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.2×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the single study of Atkinson et al. (1985). The error limits are expanded to reflect the necessity to correct for removal of ocimene by reaction with NO_2 and because the results have not been confirmed.

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical or decompose to release NO_2. At atmospheric pressure the formation of the peroxy radical will generally dominate.

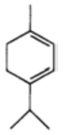
References

Atkinson, R., Aschmann, S. M., Winer, A. M. and Pitts Jr., J. N.: Env. Sci. Tech., 19, 159-163, 1985.

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605-4638, 2003.

NO_3_VOC40: α-terpinene

Last evaluated: June 2013; Last change in preferred values: June 2013

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.82 \pm 0.07) \times 10^{-10}$	294	Atkinson et al., 1985	RR-GC (a)
$(1.03 \pm 0.06) \times 10^{-10}$	298	Berndt et al., 1996	RR (b)

α-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,3-diene.

Comments

(a) 4000 L Teflon chamber at 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Correction made to the α-terpinene loss rate due to reaction with NO_2 was 10 – 47 %. α-terpinene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio, k(NO_3 + α-terpinene) / k(NO_3 + 2,3-dimethyl-2-butene) = 3.18 ± 0.13 is placed on an absolute basis using k(NO_3 + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(b) Flow tube at 15 mbar N_2. NO_3 was generated by the thermal decomposition of N_2O_5. Various detection schemes (electron impact MS, FTIR and GC-MS/FID) were available though it is not stated which was used for the relative rate analysis. The rate constant ratio obtained, k(NO_3 + α-terpinene) / k(NO_3 + 2,3-dimethyl-2-butene) = 1.796 ± 0.10 is placed on an absolute basis using k(NO_3 + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.8×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

Despite use of the same reference reactant, the two relative rate studies derive rather different rate coefficients. It is not clear whether this is due to the different pressures and bath gases used. The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1985) in which the experiments were carried out at roughly atmospheric pressure and in air. The error limits are expanded to reflect the poor agreement between the two studies and the necessity to correct for removal of α-terpinene by reaction with NO_2.

The large rate constant indicates that addition of NO_3 across a double bond to form a nitrooxy- radical is the initial step. Organic nitrates (but not peroxy-nitrates or carbonyls) have been observed in N_2/O_2 bath gas and p-cymene is observed at yields of ~6 % at pressures of N_2 or air above 100 Torr (Berndt et al., 1996).

References

Atkinson, R., Aschmann, S. M., Winer, A. M. and Pitts Jr, J. N., Env. Sci. Tech., 19, 159-163, 1985.

Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Berndt, T., Böge, O., Kind, I. and Rolle, W., Ber. Bunsenges .Phys. Chem., 100, 462-469, 1996.

NO3_VOC41: γ-terpinene

Last evaluated: June 2013; Last change in preferred values: June 2013

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.4 \pm 0.7) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$(3.6 \pm 0.7) \times 10^{-11}$	433		
Relative Rate Coefficients			
$(2.94 \pm 0.05) \times 10^{-11}$	294	Atkinson et al., 1985	RR (b)

γ-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,4-diene.

Comments

(a) NO_3 radicals (6-30 × 10^{11} molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He. γ-terpinene was present at similar concentrations (1-3 fold) to NO_3, so that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 4000 L Teflon chamber at 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. γ-terpinene and 2-methyl-2-butene (reference reactant) were monitored by GC. Correction made to the γ -terpinene loss rate due to reaction with NO_2 was <1 %. The rate constant ratio, $k(NO_3 + \gamma\text{-terpinene}) / k(NO_3 + \text{2-methyl-2-butene}) = 3.14 \pm 0.05$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.9×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.12	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1985) in which absolute determination of the reactant concentrations was not required. The error limits are expanded to reflect the necessity to correct for removal of γ-terpinene by reaction with NO_2 and the ≈ 20 % difference to the absolute rate measurement at the same temperature (Martínez et al., 1999). The difference between the rate coefficients obtained at 298 and 433 K (factor 1.5) was not considered large enough to warrant a more detailed investigation of the temperature dependence (Martínez et al., 1999).

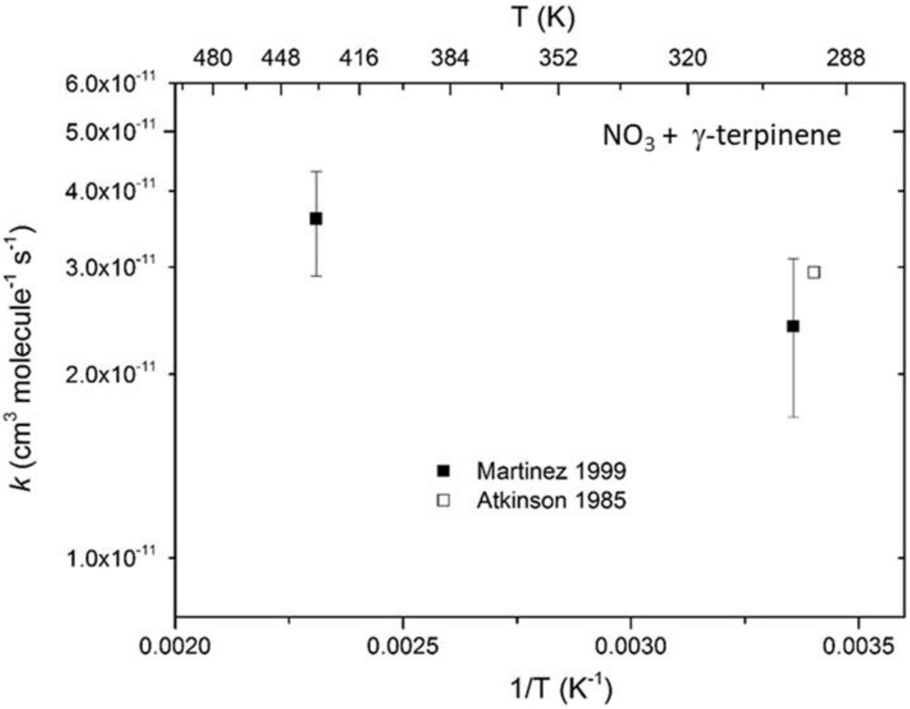
There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical or decompose to release NO_2. At atmospheric pressure the formation of the peroxy radical will generally dominate.

References

Atkinson, R., Aschmann, S. M., Winer, A. M. and Pitts, J. N., Env. Sci. Tech., 19, 159-163, 1985.

Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

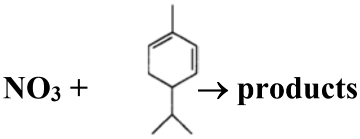
Martínez, E., Cabañas, B., Aranda, A., Martín, P. and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.



Rate coefficients for NO_3 + γ-terpinene.

NO3_VOC42: α-phellandrene

Last evaluated: June 2013; Last change in preferred values: June 2013



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(4.2 \pm 1.0) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$1.9 \times 10^{-9} \exp[-(1158 \pm 270)/T]$	298-433		
Relative Rate Coefficients			
$(8.52 \pm 0.63) \times 10^{-11}$	294	Atkinson et al., 1985	RR (b)
$(5.98 \pm 0.20) \times 10^{-11}$	298	Berndt et al., 1996	RR (c)

α-phellandrene is 2-methyl-5-(1-methylethyl)-1,3-cyclohexadiene.

Comments

(a) NO_3 radicals (6-30 × 10^{11} molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He. α-phellandrene was present at similar concentrations (1-3 fold) to NO_3, so that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 4000 L Teflon chamber at 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Correction made to the α-phellandrene loss rate due to reaction with NO_2 was 29 – 46 %. α-phellandrene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio, k(NO_3 + α-phellandrene) / k(NO_3 + 2,3-dimethyl-2-butene) = 1.49 ± 0.11 is placed on an absolute basis using k(NO_3 + 2,3-dimethyl-2-butene) = 5.72 × 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(c) Flow tube at 15 mbar N_2. NO_3 was generated by the thermal decomposition of N_2O_5, 2,3-dimethyl-2-butene was used as reference reactant. Various detection schemes (electron impact MS, FTIR and GC-MS/FID) were available though it is not stated which was used for the relative rate analysis. The rate constant ratio obtained, k(NO_3 + α-phellandrene) / k(NO_3 + 2,3-dimethyl-2-butene) = 1.046 ± 0.035 is placed on an absolute basis using k(NO_3 + 2,3-dimethyl-2-butene) = 5.72 × 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	7.3×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.15	298

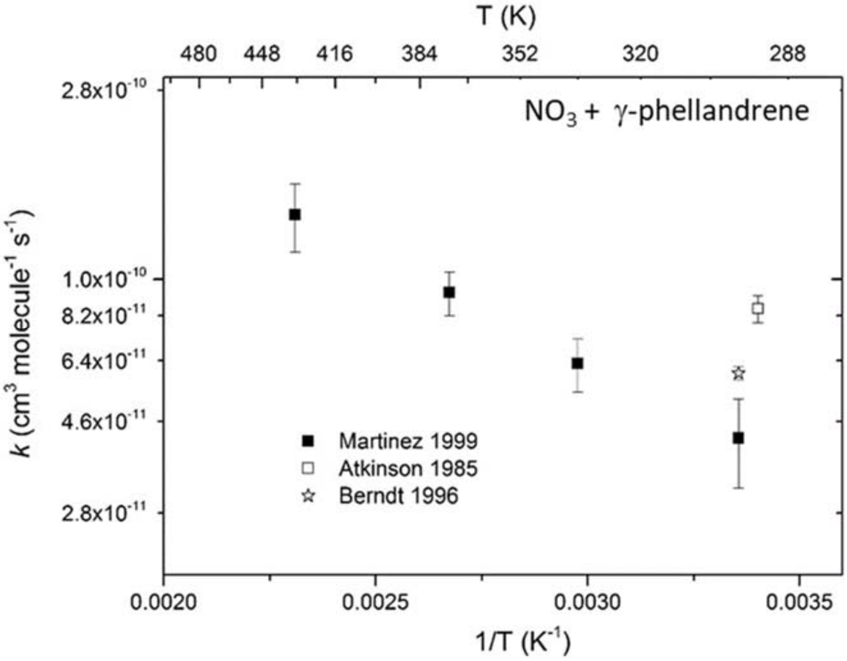
Comments on Preferred Values

The preferred value of the room temperature rate coefficient is an average of the two relative rate studies in which absolute determination of the reactant concentrations was not required. The error limits are expanded to reflect the necessity to correct for removal of α-phellandrene by reaction with NO_2 and the poor agreement between the three studies. The significant, positive dependence of k on temperature observed by Martínez et al. (1999) requires validation.

The large rate constant indicates that addition of NO_3 across a double bond to form a nitrooxyalkyl radical is the initial step. This can decompose to c-cymene, with a yield of ~ 20 % at pressures above 150 mbar N_2 or air (Berndt et al., 1996). Organic nitrates (but not peroxy-nitrates or carbonyls) have been observed in N_2/O_2 bath gas.

References

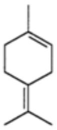
Atkinson, R., Aschmann, S. M., Winer, A. M. and Pitts Jr., J. N., Env. Sci. Tech., 19, 159-163, 1985.
Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Berndt, T., Böge, O., Kind, I. and Rolle, W., Ber. Bunsenges. Phys. Chem., 100, 462-469, 1996.
Martínez, E., Cabañas, B., Aranda, A., Martín, P. and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.



Rate coefficients for NO_3 + γ-phellandrene.

NO3_VOC43: terpinolene

Last evaluated: June 2013; Last change in preferred values: June 2013

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(5.2 \pm 0.9) \times 10^{-11}$	298	Martínez et al., 1999	DF-LIF (a)
$(7.5 \pm 1.0) \times 10^{-11}$	433		
Relative Rate Coefficients			
$(9.67 \pm 0.51) \times 10^{-11}$	295	Corchnoy and Atkinson, 1990	RR (b)
$(6.12 \pm 0.52) \times 10^{-11}$	298	Stewart et al., 2013	RR (c)

Terpinolene is 4-isopropylidene-1-methyl-cyclohexene.

Comments

(a) NO_3 radicals ($6\text{-}30 \times 10^{11}$ molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He. Terpinolene was present at similar concentrations (1-3 fold) to NO_3 and absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) 6400 L Teflon chamber at 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Terpinolene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio $k(NO_3$ + terpinolene) / ($k(NO_3$ + 2,3-dimethyl-2-butene) = 1.69 ± 0.09 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(c) 1 L glass vessel at 1013 mbar (760 Torr) of air. Relative changes in concentration of terpinolene and limonene (reference reactant) were monitored by GC. The rate constant ratio $k(NO_3$ + terpinolene) / ($k(NO_3$ + limonene) = 5.10 ± 0.43 is placed on an absolute basis using $k(NO_3$ + limonene) = 1.2×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	9.7×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.25	298

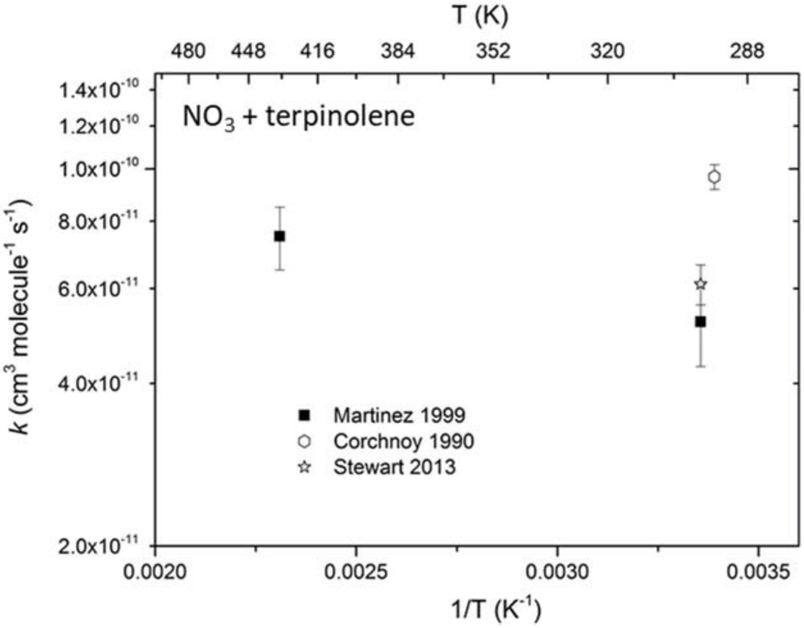
Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the relative rate study of Corchnoy and Atkinson (1990) in which absolute determination of the reactant concentrations was not required. The error limits are expanded to reflect the poor agreement with the absolute rate measurement at the same temperature (Martínez et al., 1999) and the relative rate study of Stewart et al (2013). The difference between the rate coefficients obtained at 298 and 433 K (factor 1.44) was not considered large enough to warrant a more detailed investigation of the temperature dependence (Martínez et al., 1999).

There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical or decompose to release NO_2. At atmospheric pressure the formation of the peroxy radical will generally dominate.

References

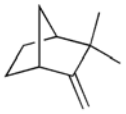
Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Corchnoy, S. B. and Atkinson, R., Env. Sci. Tech., 24, 1497-1502, 1990.
IUPAC, Task Group on Atmospheric Chemical kinetic data evaluation. (Ammann, M., Atkinson, R., Cox, R.A., Crowley, J.N., Hynes, R. G., Jenkin, M.E., Mellouki, W., Rossi, M. J., Troe, J. and Wallington, T. J.) Evaluated kinetic data: http://iupac.pole-ether.fr, 2019.
Martínez, E., Cabañas, B., Aranda, A., Martín, P. and Salgado, S., J. Atmos. Chem., 33, 265-282, 1999.
Stewart, D. J., Almabrok, S. H., Lockhart, J. P., Mohamed, O. M., Nutt, D. R., Pfrang, C. and Marston, G., Atmos. Env., 70, 227-235, 2013.



Rate coefficients for NO_3 + terpinolene.

NO3_VOC46: camphene

Last evaluated: November 2016; Last change in preferred values: November 2016

NO_3 +  → **products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(6.2 \pm 2.1) \times 10^{-13}$	298	Martínez et al., 1998	DF-LIF (a)
$3.1 \times 10^{-12} \exp[(-481 \pm 55)/T]$	298-433		
Relative Rate Coefficients			
$(6.59 \pm 0.16) \times 10^{-13}$	296	Atkinson et al., 1990	RR (b)

Camphene is 2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane.

Comments

(a) NO_3 radicals (≈ 3-6 × 10^{12} molecule cm^{-3}) generated from reaction of F atoms (made in a microwave discharge through F_2/He) with HNO_3. Flow tube was operated at ~1.33 mbar (1 Torr) He at 4 temperatures between 298 and 393 K. Camphene was present at similar concentrations (≈3-20 × 10^{12} molecule cm^{-3}) to NO_3, so that absolute NO_3 concentrations (derived by titration with tetramethylethene) were necessary to derive the rate coefficient.

(b) Loss of camphene and *trans*-2-butene (reference reactant) in a 6400 L Teflon chamber at 980 mbar (735 Torr) of air were monitored by GC following exposure to NO_3 radicals generated by the thermal decomposition of N_2O_5. The rate constant ratio, $k(NO_3 + \text{camphene}) / k(NO_3 + \textit{trans}\text{-2-butene}) = 1.69 \pm 0.04$ required correction for an impurity in the camphene sample and is placed on an absolute basis using $k(NO_3 + \textit{trans}\text{-2-butene}) = 3.9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	6.6×10^{-13}	298
Reliability		
$\Delta \log k$	± 0.10	298

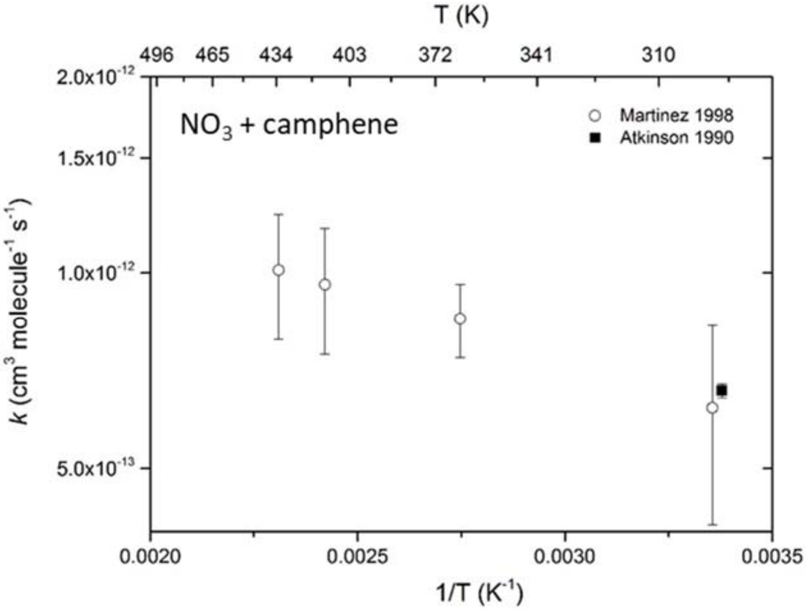
Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Atkinson et al. 1990, which agrees with the absolute study of Martínez et al. (1999). The significant, positive dependence of k on temperature observed by Martínez et al. (1999) requires validation.

There are no product studies of this reaction, though by analogy to other NO_3 + terpene reactions, the reaction will proceed mainly via addition of NO_3 across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O_2 to form a nitrooxyalkyl peroxy radical.

References

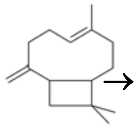
Atkinson, R., Aschmann, S. M. and Arey, J., Atmos. Env. A, 24, 2647-2654, 1990.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.
Martínez, E., Cabañas, B., Aranda, A. and Martín, P., Env. Sci. Tech., 32, 3730-3734, 1998.



Rate coefficients for the reaction NO_3 + camphene.

NO3_VOC47: β-caryophyllene

Last evaluated: June 2016; Last change in preferred values: June 2016

NO$_3$ +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.92 \pm 0.35) \times 10^{-11}$	296	Shu and Atkinson, 1995	RR (a)

β-caryophyllene is: *trans*-(1*R*,9*S*)-8-methylene-4,11,11-trimethylbicyclo[7.2.0]undec-4-ene.

Comments

(a) Relative rate of loss of β-caryophyllene and 2-methyl-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID. NO$_3$ was generated by the thermal decomposition of N$_2$O$_5$. A correction was applied to take into account loss of β-caryophyllene by reaction with NO$_2$. The rate constant ratio, k(NO$_3$ + β-caryophyllene) / k(NO$_3$ + 2-methyl-2-butene) = 2.05 ± 0.37 is placed on an absolute basis using k(NO$_3$ + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.9×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO$_3$ across a double bond to form a nitrooxyalkyl radical which can react with O$_2$ to form a nitrooxyalkyl peroxy radical.

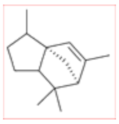
Secondary aerosol is formed efficiently in chamber studies of the NO$_3$-radical initiated oxidation of β-caryophyllene with yields (defined as the mass of aerosol formed per mass of β-caryophyllene reacted) of close to 100 % (Jaoui et al., 2013; Fry et al., 2014) with compounds of molecular weight up to *m/z* 375 identified. Product organic nitrates have low vapour pressures and have been found to partition entirely to the aerosol phase (Fry et al., 2014).

References

Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.
Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkle, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C. and Lee, L., Env. Sci. Tech., 48, 11944-11953, 2014.
Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M. and Offenberg, J. H., Environmental Chemistry, 10, 178-193, 2013.
Shu, Y. H. and Atkinson, R., J. Geophys. Res., 100, 7275-7281, 1995.

NO3_VOC48: α-cedrene

Last evaluated: June 2016; Last change in preferred values: June 2016

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.16 \pm 0.72) \times 10^{-12}$	296	Shu andAtkinson., 1995	RR (a)

α-cedrene is: (1*S*,2*R*,5*S*,7*R*)-2,6,6,8-tetramethyltricyclo[5.3.1.0^{1,5}]undec-8-ene

Comments

(a) Relative rate of loss of α-cedrene and 2-methyl-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID. NO_3 was generated by the thermal decomposition of N_2O_5. The rate constant ratio, $k(NO_3 + \alpha\text{-cedrene}) / k(NO_3 + \text{2-methyl-2-butene}) = 0.871 \pm 0.077$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	8.2×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson, 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO_3 across the double bond to form a nitrooxyalkyl radical which can react with O_2 to form a nitrooxyalkyl peroxy radical.

Secondary aerosol is formed efficiently in chamber studies of the NO_3-radical initiated oxidation of α-cedrene (Jaoui et al., 2013).

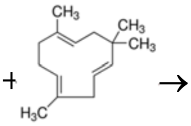
References

Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.

Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M. and Offenberg, J. H., Environ. Chem., 10, 178-193, 2013.
Shu, Y. H. and Atkinson, R., J. Geophys. Res., 100, 7275-7281, 1995.

NO3_VOC49: α-humulene

Last evaluated: June 2016; Last change in preferred values: June 2016

NO_3 +  → **products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(3.53 \pm 0.26) \times 10^{-11}$	296	Shu and Atkinson, 1995	RR (a)

α-humulene is: (1E,4E,8E)-2,6,6,9-tetramethylcycloundeca-1,4,8-triene

Comments

(a) Loss of α-humulene and 2-methyl-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID. NO_3 was generated by the thermal decomposition of N_2O_5. The rate constant ratio, k(α-humulene) / k(NO_3 + 2-methyl-2-butene) = 3.77 ± 0.28 is placed on an absolute basis using k(NO_3 + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.5×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson, 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO_3 across the double bond to form a nitrooxyalkyl radical which can react with O_2 to form a nitrooxyalkyl peroxy radical.

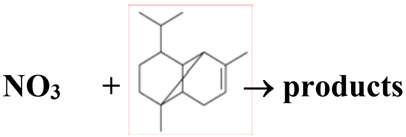
Secondary aerosol is formed efficiently in chamber studies of the NO_3-radical initiated oxidation of α-humulene (Jaoui et al., 2013).

References

Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.
Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M. and Offenberg, J. H., Environ. Chem., 10, 178-193, 2013.
Shu, Y. H. and Atkinson, R., J. Geophys. Res. Atmos., 100, 7275-7281, 1995.

NO3_VOC50: α-copaene

Last evaluated: June 2016; Last change in preferred values: June 2016



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.61 \pm 0.07) \times 10^{-11}$	296	Shu and Atkinson, 1995	RR (a)

α -copaene is: (1*R*,2*S*,6*S*,7*S*,8*S*)-8-isopropyl-1,3-dimethyltricyclo[4.4.0.0^{2,7}]dec-3-ene.

Comments

(a) Loss of α-copaene and 2-methyl-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID on exposure to NO_3 radicals. NO_3 was generated by the thermal decomposition of N_2O_5. The rate constant ratio, $k(NO_3 + \alpha\text{-copaene}) / k(NO_3 + \text{2-methyl-2-butene}) = 1.72 \pm 0.08$ is placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.6×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson 1991).

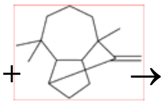
There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO_3 across the double bond to form a nitrooxyalkyl radical which can react with O_2 to form a nitrooxyalkyl peroxy radical.

References

Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.
Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Shu, Y. H. and Atkinson, R., J. Geophys. Res., 100, 7275-7281, 1995.

NO3_VOC51: longifolene

Last evaluated: June 2016; Last change in preferred values: June 2016

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(6.79 \pm 0.47) \times 10^{-13}$	296	Shu and Atkinson, 1995	RR (a)

longifolene is: (1*R*,2*S*,7*S*,9*S*)- 3,3,7-trimethyl- 8-methylenetricyclo- [5.4.0.0^{2,9}]undecane.

Comments

(a) Loss of longifolene and *trans*-2-butene (reference reactant) in a 6700 L Teflon chamber at 987 mbar (740 Torr) of air were monitored by GC-FID on exposure to NO_3 radicals. NO_3 was generated by the thermal decomposition of N_2O_5. The rate constant ratio, $k(NO_3$ + longifolene) / $k(NO_3$ + *trans*-2-butene) = 1.74 ± 0.12 is placed on an absolute basis using $k(NO_3$ + *trans*-2-butene) = 3.9×10^{-13} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	6.8×10^{-13}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Shu and Atkinson (1995). The error limits have been expanded to reflect the fact that this is the only study available. The rate coefficient is consistent with estimates based on the number of double bonds and the number and position of the alkyl substituents (Atkinson 1991).

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO_3 across the double bond to form a nitrooxyalkyl radical which can react with O_2 to form a nitrooxyalkyl peroxy radical.

References

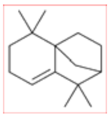
Atkinson, R., J. Phys. Chem. Ref. Data, 20, 459-507, 1991.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

Shu, Y. H. and Atkinson, R., J. Geophys. Res., 100, 7275-7281, 1995.

NO3_VOC52: isolongifolene

Last evaluated: June 2016; Last change in preferred values: June 2016

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(3.89 \pm 0.41) \times 10^{-12}$	298 ± 2	Canosa-Mas et al., 1999	RR (a)

isolongifolene is: 2,2,7,7-tetramethyltricyclo[6.2.1.0$^{1.6}$]undec-5-ene.

Comments

(a) Loss of isolongifolene and α-pinene (reference reactant) in a 56 L Teflon bag at 1013 mbar (760 Torr) of N_2 were monitored by GC-FID following exposure to NO_3 radicals generated by the thermal decomposition of N_2O_5. The rate constant ratio, $k(NO_3 + \text{isolongifolene}) / k(NO_3 + \alpha\text{-pinene}) = 0.627 \pm 0.066$ is placed on an absolute basis using $k(NO_3 + \alpha\text{-pinene}) = 6.2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.9×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Canosa-Mas et al. (1999). The error limits have been expanded to reflect the fact that this is the only study available.

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO_3 across the double bond to form a nitrooxyalkyl radical which can react with O_2 to form a nitrooxyalkyl peroxy radical.

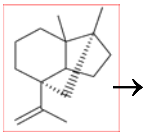
References

Canosa-Mas, C. E., King, M. D., Scarr, P. J., Thompson, K. C. and Wayne, R. P., Phys. Chem. Chem. Phys., 1, 2929-2933, 1999.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

NO3_VOC53: alloisolongifolene

Last evaluated: June 2016; Last change in preferred values: June 2016

NO_3 +  → **products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.41 \pm 0.24) \times 10^{-12}$	298 ± 2	Canosa-Mas et al., 1999	RR (a)

alloisolongifolene is: (4R,7aS)-1,7a-dimethyl-4-(prop-1-en-2-yl)octahydro-1H-1,4-methanoindene.

Comments

(a) Loss of alloisolongifolene and cyclohexa-1,4-diene (reference reactant) in a 56 L Teflon bag at 1013 mbar (760 Torr) of N_2 were monitored by GC-FID following exposure to NO_3 radicals generated by the thermal decomposition of N_2O_5. The rate constant ratio, $k(NO_3 + \text{alloisolongifolene}) / k(NO_3 + \text{cyclohexa-1,4-diene}) = 2.14 \pm 0.37$ is placed on an absolute basis using $k(NO_3 + \text{cyclohexa-1,4-diene}) = 6.6 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.4×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Canosa-Mas et al. (1999). The error limits have been expanded to reflect the fact that this is the only study available.

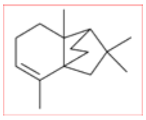
There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO_3 across the double bond to form a nitrooxyalkyl radical which can react with O_2 to form a nitrooxyalkyl peroxy radical.

References

Atkinson, R. and Arey, J., Chem. Rev., 103, 4605-4638, 2003.
Canosa-Mas, C. E., King, M. D., Scarr, P. J., Thompson, K. C. and Wayne, R. P., Phys. Chem. Chem. Phys., 1, 2929-2933, 1999.

NO3_VOC54: α-neoclovene

Last evaluated: June 2016; Last change in preferred values: June 2016

NO_3 +  **→ products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(8.25 \pm 2.1) \times 10^{-12}$	298 ± 2	Canosa-Mas et al., 1999	RR (a)

α-neoclovene is: (1S,7aS)-1,2,3,6,7,7a-hexahydro-2,2,4,7a-tetramethyl-1,3a-ethano-3aH-indene.

Comments

(a) Loss of α-neoclovene and α-pinene (reference reactant) in a 56 L Teflon bag at 1013 mbar (760 Torr) of N_2 were monitored by GC-FID following exposure to NO_3 radicals generated by the thermal decomposition of N_2O_5. Significant loss of α-neoclovene was observed in the absence of NO_3 and correction was applied. The resulting rate constant ratio, k(NO_3 + α-neoclovene) / k(NO_3 + α-pinene) = 1.33 ± 0.34 is placed on an absolute basis using k(NO_3 + α-pinene) = 6.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	8.25×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Canosa-Mas et al. (1999). The error limits have been expanded to reflect the fact that this is the only study available.

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO_3 across the double bond to form a nitrooxyalkyl radical which can react with O_2 to form a nitrooxyalkyl peroxy radical.

References

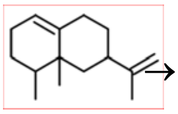
Canosa-Mas, C. E., King, M. D., Scarr, P. J., Thompson, K. C. and Wayne, R. P., Phys. Chem. Chem. Phys., 1, 2929-2933, 1999.

IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

NO3_VOC55: valencene

Last evaluated: June 2016; Last change in preferred values: June 2016

NO_3 +



→ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(7.9 \pm 0.2) \times 10^{-12}$	298 ± 2	Ham, 2013.	RR (a)

valencene is: (2*R*)-8,8, 8a-trimethyl-2-prop-1-en-2-yl- 1,2,3,4,6,7-hexahydronaphthalene.

Comments

(a) Loss of valencene and 3-carene or limonene (reference reactants) in a ≈ 100 L Teflon bag at atmospheric pressure of air were monitored by GC-MS following exposure to NO_3 radicals generated by the thermal decomposition of N_2O_5. The measured rate coefficient ratios were not reported. Ham (2013) used reference rate coefficients for NO_3 + 3-carene (9.1×10^{-12} cm^3 molecule^{-1} s^{-1}) and NO_3 + limonene (1.22×10^{-11} cm^3 molecule^{-1} s^{-1}) that agree with present IUPAC recommendations (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	7.9×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is based on the relative rate study of Ham, (2013). The error limits have been expanded to reflect the fact that this is the only study available.

There are no studies of the gas-phase products of this reaction, though it is expected to proceed predominantly via addition of NO_3 across the double bond to form a nitrooxyalkyl radical which can react with O_2 to form a nitrooxyalkyl peroxy radical.

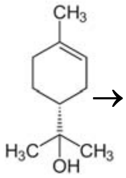
References

Ham, J. E., Int. J. Chem. Kinet., 45, 508-514, 2013.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

NO3_VOC56: α-terpineol

Last evaluated: June 2018; Last change in preferred values: June 2018

NO_3 +



→ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.9 \pm 0.2) \times 10^{-11}$	297 ± 3	Jones and Ham, 2008.	RR (a)
$(1.6 \pm 0.2) \times 10^{-11}$			RR (b)

α-terpineol is: (2-(4-methyl-1-cyclohex-3-enyl)propan-2-ol.

Comments

(a) Loss of α-terpineol and either 2-carene or 3-carene (reference reactants) in a ≈ 65 L Teflon bag at atmospheric pressure of air were monitored by GC-MS following exposure to NO_3 radicals generated by the thermal decomposition of N_2O_5. The rate coefficient ratio k(α-terpineol) / k(2-carene) = 0.95 ± 0.02 was put on an absolute basis using k(2-carene) = 2.0×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(b) See note (a). k(α-terpineol)/k(3-carene) = 1.76 ± 0.02 was put on an absolute basis using k(3-carene) = 9.1×10^{-12} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.7×10^{-11}	298
Reliability		
Δ log k	± 0.25	298

Comments on Preferred Values

The preferred value at 298 K is an averge of the relative rate studies of Jones and Ham, (2008). The error limits have been expanded to reflect the fact that this is the only study available.

Jones and Ham (2008) identified carbonyls, dicarbonyls and hydroxy-nitrates as the products of the reaction between NO_3 and terpineol, concluding that both addition of NO_3 to the double bond as well as abstraction of the tertiary H-atom take place. Yields were not reported.

References

Jones, B.T., and Ham, J. E., Atmos. Env., 42, 6689-6698, 2008.
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NO3_AROM1: benzene

Last evaluated: September 2008; Last change in preferred values: September 2008

$NO_3 + C_6H_6 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$\leq 5 \times 10^{-17}$	300	Japar and Niki, 1975	RR-FTIR (a)
$\leq 2.7 \times 10^{-17}$	298 ± 1	Atkinson et al., 1984a	RR-FTIR (b)
$<6 \times 10^{-17}$	298 ± 1	Atkinson et al., 1984b	RR-FTIR (c)

Comments

(a) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The experimental data were relative to the equilibrium coefficient K for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis using $K = 2.15 \times 10^{-11}$ cm^3 molecule^{-1} at 300 K (IUPAC, 2019).

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of benzene and ethene (the reference compound) were measured by GC, and a rate coefficient ratio of $k(NO_3$ + benzene$)/k(NO_3$ + ethene$) \leq 0.13$ was obtained. This rate coefficient ratio is placed on an absolute basis using $k(NO_3$ + ethene$) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of toluene and *n*-heptane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(NO_3$ + benzene$)/k(NO_3$ + *n*-heptane$) <0.4$ is placed on an absolute basis using $k(NO_3$ + *n*-heptane$) = 1.5 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	$< 3 \times 10^{-17}$	298

Comments on Preferred Values

All three room temperature relative rate measurements (Japar and Niki, 1975; Atkinson et al., 1984a,b) obtained only upper limits to the rate coefficient. These studies are the basis for the preferred value.

References

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Japar, S. M. and Niki, H.: J. Phys. Chem., 79, 1629, 1975.

$NO_3 + C_6H_5CH_3 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$\leq 5 \times 10^{-17}$	300	Japar and Niki, 1975	RR-FTIR (a)
$\leq 3.8 \times 10^{-15}$	300 ± 1	Carter et al., 1981	RR-GC (b)
$(6.7 \pm 2.6) \times 10^{-17}$	298 ± 1	Atkinson et al., 1984a	RR-GC (c)
$(6.75 \pm 1.65) \times 10^{-17}$	298 ± 1	Atkinson et al., 1984b	RR-GC (d)
$(7.81 \pm 0.83) \times 10^{-17}$	296 ± 2	Atkinson and Aschmann, 1988	RR-GC (d)

Comments

(a) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The experimental data were relative to the equilibrium coefficient K for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions, and are placed on an absolute basis by use of $K = 2.15 \times 10^{-11}$ cm^3 molecule^{-1} at 300 K (IUPAC, 2019).

(b) NO_3 radicals were generated from the reaction of O_3 with NO_2 in the presence of toluene and propene (the reference compound). The contribution of the O_3 reaction was taken into account in estimating the amount of propene reacted with NO_3 radicals. The concentrations of toluene and propene were monitored by GC, and the derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{propene}) = 9.79 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 300 K (IUPAC, 2019).

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of toluene and ethene (the reference compound) were measured by GC, and a rate coefficient ratio of $k(NO_3 + \text{toluene})/k(NO_3 + \text{ethene}) = 0.32 \pm 0.12$ obtained. This rate coefficient ratio is placed on an absolute basis using $k(NO_3 + \text{ethene}) = 2.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K (IUPAC, 2019).

(d) NO_3 radicals were generated from the thermal decomposition of N_2O_5. The concentrations of toluene and *n*-heptane (the reference compound) were measured by GC. Rate coefficient ratios of $k(NO_3 + \text{toluene})/k(NO_3 + n\text{-heptane}) = 0.45 \pm 0.11$ (Atkinson et al., 1984b) and 0.57 ± 0.06 (Atkinson and Aschmann, 1988) were obtained. These rate coefficient ratios are placed on an absolute basis by use of rate coefficients of $k(NO_3 + n\text{-heptane}) = 1.37 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 296 K (Atkinson, 1991) and 1.5×10^{-16} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003). Rate coefficient ratios of $k(NO_3 + C_6H_5CD_3)/k(NO_3 + n\text{-heptane}) = 0.28 \pm 0.05$ and $k(NO_3 + C_6D_5CD_3)/k(NO_3 + n\text{-heptane}) = 0.25 \pm 0.13$ at 296 ± 2 K were also determined by Atkinson and Aschmann (1988).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	7.8×10^{-17}	298
Reliability		
$\Delta \log k$	± 0.25	298

Comments on Preferred Values

The room temperature relative rate measurements of Atkinson et al. (1984a, 1984b) and Atkinson and Aschmann (1988) are in good agreement and are consistent with the upper limit of Carter et al. (1981). While the upper limit to the rate coefficient obtained by Japar and Niki (1975) relative to the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions is somewhat lower than the rate coefficients of Atkinson et al. (1984a,b) and Atkinson and Aschmann (1988), there are significant uncertainties in the equilibrium constant used for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions. The preferred 298 K value is based on the most recent study of Atkinson and Aschmann (1988). In that study, rate coefficients were also measured for the reactions of NO_3 radicals with $C_6H_5CD_3$ and $C_6D_5CD_3$, and the significant deuterium isotope effect for the $C_6H_5CD_3$ reaction indicates that the reaction proceeds by H- (or D-) atom abstraction from the CH_3 (or CD_3) substituent group.

$$NO_3 + C_6H_5CH_3 \rightarrow HNO_3 + C_6H_5CH_2$$

This conclusion is consistent with the trend in reaction rate coefficients for the reactions of NO_3 radicals with toluene, the xylenes and the trimethylbenzenes (Atkinson, 1991).

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NO3_AROM3: *m*-cresol

Last evaluated: September 2008; Last change in preferred values: September 2008

$$\mathbf{NO_3 + \textit{m}\text{-}CH_3C_6H_4OH \rightarrow CH_3C_6H_4O + HNO_3 \quad (1)}$$
$$\mathbf{\rightarrow \text{other products} \quad (2)}$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(8.10 \pm 1.16) \times 10^{-12}$	300 ± 1	Carter et al., 1981	RR-GC (a)
$(1.66 \pm 0.18) \times 10^{-11}$	298 ± 1	Atkinson et al., 1984	RR-FTIR (b)
$\sim 1.33 \times 10^{-11}$	298 ± 1	Atkinson et al., 1984	RR-FTIR (c)
$(9.74 \pm 0.47) \times 10^{-12}$	296 ± 2	Atkinson et al., 1992	RR-GC (d)

Comments

(a) NO_3 radicals were generated from the reaction of O_3 with NO_2 in the presence of *m*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The contribution of the O_3 reaction was taken into account in estimating the amount of 2-methyl-2-butene reacted with NO_3 radicals. The concentrations of *m*-cresol and 2-methyl-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5 in the presence of *m*-cresol and phenol (the reference compound) at atmospheric pressure of air. The concentrations of *m*-cresol and phenol were monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(NO_3 + m\text{-cresol})/k(NO_3 + \text{phenol}) = 4.36 \pm 0.46$ is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{phenol}) = 3.8 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5 at atmospheric pressure of air. The concentrations of *m*-cresol, N_2O_5 and NO_2 were monitored by FTIR spectroscopy. The rate coefficient for NO_3 + *m*-cresol was measured relative to the equilibrium coefficient K for the reactions $NO_2 + NO_3 \leftrightarrow N_2O_5$. The experimental data are placed on an absolute basis by use of an equilibrium coefficient of $K = 2.75 \text{ x } 10^{-11}$ cm^3 molecule^{-1} at 298 K (IUPAC, 2019). Evidence for secondary reactions removing *m*-cresol observed.

(d) NO_3 radicals were generated from the thermal decomposition of N_2O_5 in the presence of *m*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of *m*-cresol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratio of $k(NO_3 + m\text{-cresol})/k(NO_3 + \text{2-methyl-2-butene}) = 1.04 \pm 0.05$ is placed on an absolute basis using a rate coefficient of $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

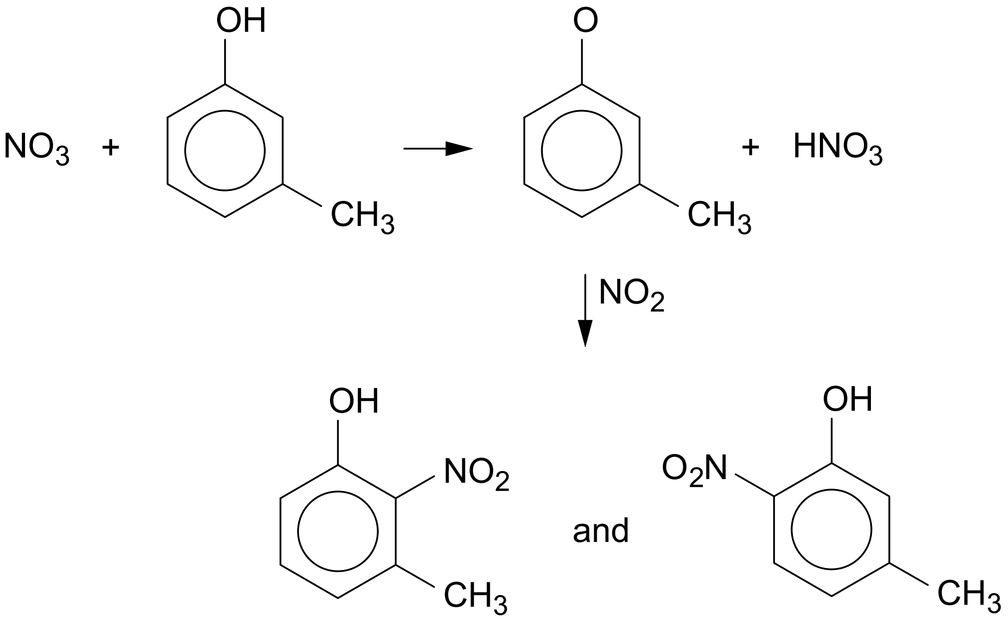
Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The reported rate coefficients are all from relative rate studies conducted at room temperature, and range over a factor of 2. The rate coefficient of Carter et al. (1981) and that of Atkinson et al. (1984) relative to the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions are subject to significant uncertainties because of the concurrent reaction of O_3 with 2-methyl-2-butene in the Carter et al. (1981) study and the uncertainties in the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions in the Atkinson et al. (1984) study. The rate coefficient measured by Atkinson et al. (1984) relative to NO_3 + phenol is a factor of 1.7 higher than that of Atkinson et al. (1992), possibly due to difficulties in determining the small amounts of phenol reacted (Atkinson et al., 1984). The preferred value is based on the study of Atkinson et al. (1992) in which the rate coefficient was measured relative to that for NO_3 + 2-methyl-2-butene. The approximate (and potentially upper limit) rate coefficient of Atkinson et al. (1984) measured relative to the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions is in reasonable agreement with the preferred value, as is that of Carter et al. (1981).

Atkinson et al. (1992) observed the formation of 3-methyl-2-nitrophenol and 5-methyl-2-nitrophenol in 16.8 ± 2.9% and 19.6 ± 3.6% yields, respectively. 3- and 5-methyl-2-nitrophenol formation is believed to arise from methylphenoxy + NO_2, and the measured 3- and 5-methyl-2-nitrophenol yields of Atkinson et al. (1992) therefore suggest that channel (1) accounts for at least 36 ± 5% of the overall reaction.



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NO3_AROM4: *o*-cresol

Last evaluated: September 2008; Last change in preferred values: September 2008

$$\mathbf{NO_3 + \textit{o}\text{-}CH_3C_6H_4OH \rightarrow CH_3C_6H_4O + HNO_3} \quad (1)$$

$$\mathbf{\rightarrow \text{other products}} \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.39 \pm 0.24) \times 10^{-11}$	300 ± 1	Carter et al., 1981	RR-GC (a)
$(1.30 \pm 0.14) \times 10^{-11}$	298 ± 1	Atkinson et al., 1984	RR-GC (b)
$(1.37 \pm 0.09) \times 10^{-11}$	296 ± 2	Atkinson et al., 1992	RR-GC (c)

Comments

(a) NO_3 radicals were generated from the reaction of O_3 with NO_2 in the presence of *o*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The contribution of the O_3 reaction was taken into account in estimating the amount of 2-methyl-2-butene reacted with NO_3 radicals. The concentrations of *o*-cresol and 2-methyl-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of k(NO_3 + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5 in the presence of *o*-cresol and *m*-cresol (the reference compound) at atmospheric pressure of air. The concentrations of *o*- and *m*-cresol were monitored by GC. The measured rate coefficient ratio of k(NO_3 + *o*-cresol)/k(NO_3 + *m*-cresol) = 1.30 ± 0.14 is placed on an absolute basis using a rate coefficient of k(NO_3 + *m*-cresol) = 1.0×10^{-11} cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5 in the presence of *o*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of *o*-cresol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratio of k(NO_3 + *o*-cresol)/k(NO_3 + 2-methyl-2-butene) = 1.46 ± 0.09 is placed on an absolute basis using a rate coefficient of k(NO_3 + 2-methyl-2-butene) = 9.37×10^{-12} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

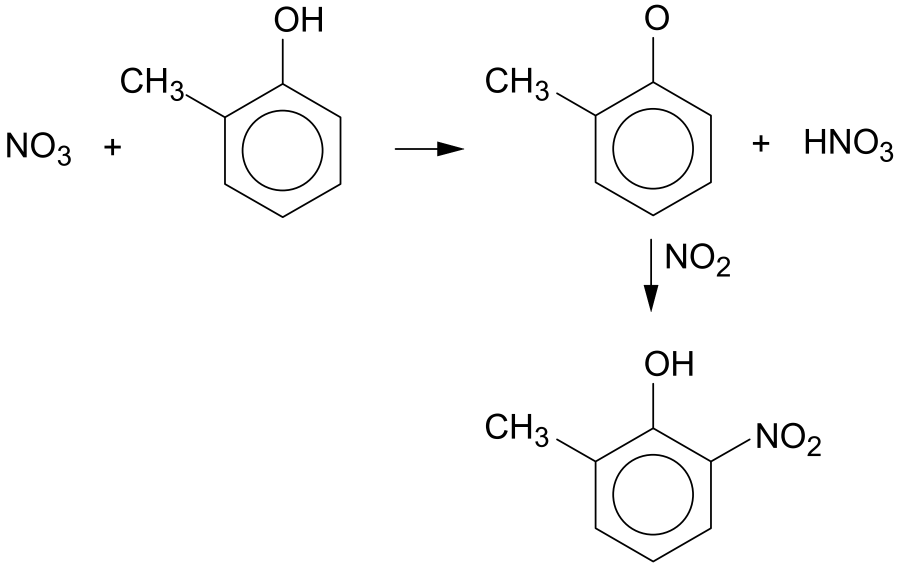
Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.4×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The reported rate coefficients are all from relative rate studies conducted at room temperature, and are in very good agreement. The preferred value is based on the study of Atkinson et al. (1992) in which the rate coefficient was measured relative to that for NO_3 + 2-methyl-2-butene. The good agreement of the rate coefficient of Atkinson et al. (1984) relative to that for NO_3 + *m*-cresol with the preferred value is gratifying, showing good self-consistency between the recommended rate coefficients for the reactions of NO_3 radicals with *o*- and *m*-cresol.

Atkinson et al. (1992) observed the formation of 6-methyl-2-nitrophenol in 12.8 ± 2.8% yield. 6-Methyl-2-nitrophenol formation is believed to arise from methylphenoxy + NO_2, and the measured 6-methyl-2-nitrophenol yield of Atkinson et al. (1992) therefore suggests that channel (1) accounts for at least 13 ± 3% of the overall reaction.



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NO3_AROM5: *p*-cresol

Last evaluated: September 2008; Last change in preferred values: September 2008

$$\mathbf{NO_3 + \mathit{p}\text{-}CH_3C_6H_4OH \rightarrow CH_3C_6H_4O + HNO_3} \quad (1)$$
$$\mathbf{\rightarrow \text{other products}} \quad (2)$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.50 \pm 0.24) \times 10^{-11}$	300 ± 1	Carter et al., 1981	RR-GC (a)
$(1.38 \pm 0.15) \times 10^{-11}$	298 ± 1	Atkinson et al., 1984	RR-GC (b)
$(1.07 \pm 0.10) \times 10^{-11}$	296 ± 2	Atkinson et al., 1992	RR-GC (c)

Comments

(a) NO_3 radicals were generated from the reaction of O_3 with NO_2 in the presence of *p*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The contribution of the O_3 reaction was taken into account in estimating the amount of 2-methyl-2-butene reacted with NO_3 radicals. The concentrations of *p*-cresol and 2-methyl-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(NO_3$ + 2-methyl-2-butene$) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5 in the presence of *p*-cresol and *m*-cresol (the reference compound) at atmospheric pressure of air. The concentrations of *p*- and *m*-cresol were monitored by GC. The measured rate coefficient ratio of $k(NO_3 + p\text{-cresol})/k(NO_3 + m\text{-cresol}) = 1.38 \pm 0.15$ is placed on an absolute basis using a rate coefficient of $k(NO_3 + m\text{-cresol}) = 1.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (IUPAC, 2019).

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5 in the presence of *p*-cresol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of *p*-cresol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratio of $k(NO_3 + p\text{-cresol})/k(NO_3 + \text{2-methyl-2-butene}) = 1.14 \pm 0.10$ is placed on an absolute basis using a rate coefficient of $k(NO_3$ + 2-methyl-2-butene$)$ $= 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

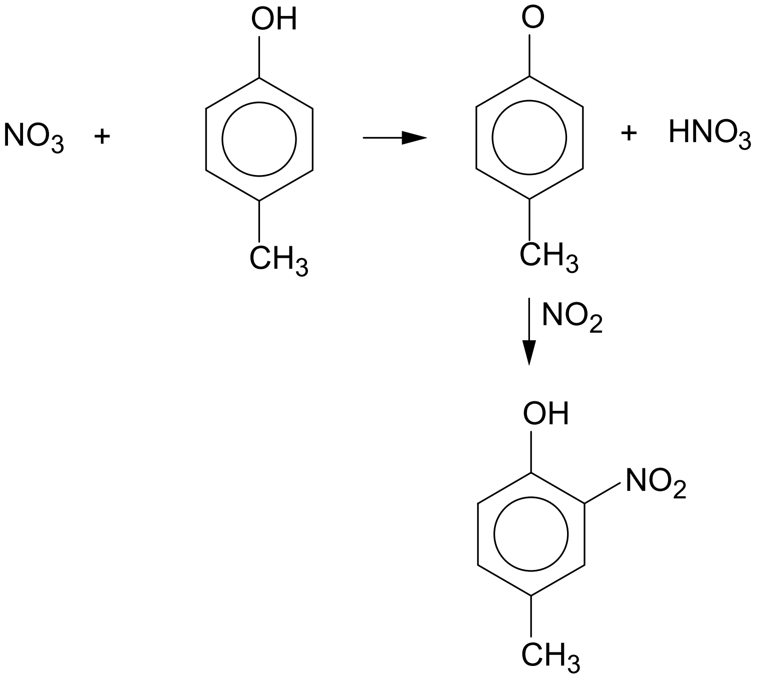
Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.1×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The reported rate coefficients are all from relative rate studies conducted at room temperature, and are in reasonable agreement. The rate coefficient of Carter et al. (1981) is subject to some uncertainties because of the concurrent reaction of O_3 with 2-methyl-2-butene. The preferred value is based on the study of Atkinson et al. (1992) in which the rate coefficient was measured relative to that for NO_3 + 2-methyl-2-butene.

Atkinson et al. (1992) observed the formation of 4-methyl-2-nitrophenol in 74 ± 16% yield. 4-Methyl-2-nitrophenol formation is believed to arise from methylphenoxy + NO_2, and the measured 4-methyl-2-nitrophenol yield of Atkinson et al. (1992) therefore suggests that channel (1) accounts for at least 76 ± 16% of the overall reaction.



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NO3_AROM6: phenol

Last evaluated: September 2008; Last change in preferred values: September 2008

$$\mathbf{NO_3 + C_6H_5OH \rightarrow C_6H_5O + HNO_3 \qquad (1)}$$

$$\mathbf{\rightarrow \text{other products} \qquad (2)}$$

Rate coefficient data ($k = k_1 + k_2$)

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(2.61 \pm 0.53) \times 10^{-12}$	300 ± 1	Carter et al., 1981	RR-GC (a)
$(3.64 \pm 0.14) \times 10^{-12}$	294	Atkinson et al., 1984	RR-GC (b)
$(4.78 \pm 0.52) \times 10^{-12}$	298 ± 1	Atkinson et al., 1984	RR-FTIR (c)
$(3.92 \pm 0.25) \times 10^{-12}$	296 ± 2	Atkinson et al., 1992	RR-GC (b)
$(5.81 \pm 1.13) \times 10^{-12}$	295 ± 2	Bolzacchini et al., 2001	RR-GC (b)

Comments

(a) NO_3 radicals were generated from the reaction of O_3 with NO_2 in the presence of phenol and *cis*-2-butene (the reference compound) at atmospheric pressure of air. The contribution of the O_3 reaction was taken into account in estimating the amount of *cis*-2-butene reacted with NO_3 radicals. The concentrations of phenol and *cis*-2-butene were monitored by GC. The derived rate coefficient ratio is placed on an absolute basis using $k(NO_3 + cis\text{-2-butene}) = 3.52 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) NO_3 radicals were generated from the thermal decomposition of N_2O_5 in the presence of phenol and 2-methyl-2-butene (the reference compound) at atmospheric pressure of air. The concentrations of phenol and 2-methyl-2-butene were monitored by GC. The measured rate coefficient ratios of $k(NO_3 + \text{phenol})/k(NO_3 + \text{2-methyl-2-butene}) = 0.389 \pm 0.014$ (Atkinson et al., 1984), 0.418 ± 0.026 (Atkinson et al., 1992) and 0.62 ± 0.12 (Bolzacchini et al., 2001) are placed on an absolute basis using $k(NO_3 + \text{2-methyl-2-butene}) = 9.37 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(c) NO_3 radicals were generated from the thermal decomposition of N_2O_5 at atmospheric pressure of air. The concentrations of phenol, N_2O_5 and NO_2 were monitored by FTIR spectroscopy. The rate coefficient for NO_3 + phenol was measured relative to the equilibrium coefficient K for the reactions $NO_2 + NO_3 \leftrightarrow N_2O_5$. The experimental data are placed on an absolute basis using $K = 2.75 \times 10^{-11}$ cm^3 molecule^{-1} at 298 K (IUPAC, 2019).

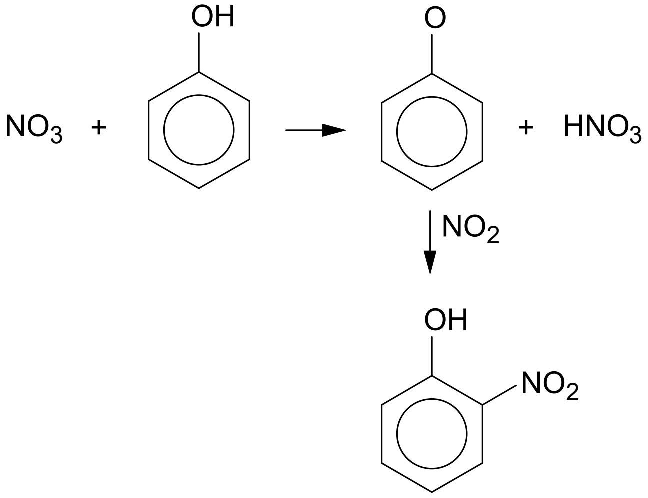
Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	3.8×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The reported rate coefficients are all from relative rate studies conducted at room temperature. The rate coefficient of Carter et al. (1981) and that of Atkinson et al. (1984) relative to the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions are subject to significant uncertainties because of the concurrent reaction of O_3 with 2-methyl-2-butene in the Carter et al. (1981) study and the uncertainties in the equilibrium constant for the $NO_3 + NO_2 \leftrightarrow N_2O_5$ reactions in the Atkinson et al. (1984) study. The preferred value is based on the studies of Atkinson et al. (1984; 1992) in which the rate coefficients were measured relative to those for NO_3 + alkene (2-methyl-2-butene in both studies) and used the thermal decomposition of N_2O_5 to generate NO_3 radicals.

Atkinson et al. (1992) observed the formation of 2-nitrophenol in 25.1 ± 5.1% yield. 2-Nitrophenol formation is believed to arise from phenoxy + NO_2, and the measured 2-nitrophenol yield of Atkinson et al. (1992) therefore suggests that channel (1) accounts for at least 25 ± 5% of the overall reaction.



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Carter, W. P. L., Winer, A. M. and Pitts Jr., J. N.: Environ. Sci. Technol., 15, 829, 1981.
IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation (Ammann, M., Cox, R.A., Crowley, J.N., Herrmann, H., Jenkin, M.E., McNeill, V.F., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.), http://iupac.pole-ether.fr/index.html., 2019.

NO3_AROM7: 1,2-dihydroxybenzene

Last evaluated: November 2008; Last change in preferred values: November 2008

$NO_3 + 1,2\text{-}C_6H_4(OH)_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(9.03 \pm 0.41) \times 10^{-11}$	298 ± 2	Olariu et al., 2004	RR-FTIR (a)
$(1.08 \pm 0.07) \times 10^{-10}$	296 ± 2	Olariu et al., 2004	RR-FTIR (b)

Comments

(a) NO_3 radicals generated by the thermal decomposition of N_2O_5. Experiments were carried out in a 1080 L chamber at 1 bar of air. The concentrations of 1,2-dihydroxybenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxybenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxybenzene loss rate due to NO_3 radical reaction during the experiments. The measured rate coefficient ratio of $k(NO_3$ + 1,2-dihydroxybenzene)/$k(NO_3$ + 2,3-dimethyl-2-butene) = 1.58 ± 0.07 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) NO_3 radicals generated by the thermal decomposition of N_2O_5. Experiments were carried out in the ~200 m^3 EUPHORE chamber at atmospheric pressure of air. The concentrations of 1,2-dihydroxybenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxybenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxybenzene loss rate due to NO_3 radical reaction during the experiments. The measured rate coefficient ratio of $k(NO_3$ + 1,2-dihydroxybenzene)/$k(NO_3$ + 2,3-dimethyl-2-butene) = 1.88 ± 0.11 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	9.9×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

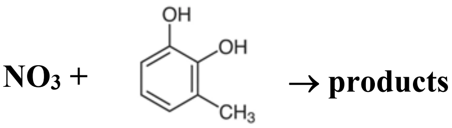
The rate coefficients measured by Olariu et al. (2004) at 296-298 K in two reaction chambers differing in volume by a factor of ~200 using a relative rate method agree to within 20%. The 298 K preferred value is an average of the two values of Olariu et al. (2004). The assigned uncertainty reflects the fact that all of the data are from a single study.

References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Olariu, R. I., Bejan, I., Barnes, I., Klotz, B., Becker, K. H. and Wirtz, K: Int. J. Chem. Kinet., 36, 577, 2004.

NO3_AROM8: 1,2-dihydroxy-3-methylbenzene

Last evaluated: November 2008; Last change in preferred values: November 2008



Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.72 \pm 0.06) \times 10^{-10}$	298 ± 2	Olariu et al., 2004	RR-FTIR (a)
$(1.68 \pm 0.04) \times 10^{-10}$	296 ± 2	Olariu et al., 2004	RR-FTIR (b)

Comments

(a) NO_3 radicals generated by the thermal decomposition of N_2O_5. Experiments were carried out in a 1080 L chamber at 1 bar of air. The concentrations of 1,2-dihydroxy-3-methylbenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-3-methylbenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxy-3-methylbenzene loss rate due to NO_3 radical reaction during the experiments. The measured rate coefficient ratio of k(NO_3 + 1,2-dihydroxy-3-methylbenzene)/k(NO_3 + 2,3-dimethyl-2-butene) = 3.01 ± 0.10 is placed on an absolute basis using k(NO_3 + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) NO_3 radicals generated by the thermal decomposition of N_2O_5. Experiments were carried out in the ~200 m^3 EUPHORE chamber at atmospheric pressure of air. The concentrations of 1,2-dihydroxy-3-methylbenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-3-methylbenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxy-3-methylbenzene loss rate during the experiments. The measured rate coefficient ratio of k(NO_3 + 1,2-dihydroxy-3-methylbenzene)/k(NO_3 + 2,3-dimethyl-2-butene) = 2.93 ± 0.06 is placed on an absolute basis using k(NO_3 + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.7×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The two rate coefficients measured by Olariu et al. (2004) at 296-298 K in two reaction chambers differing in volume by a factor of ~200 using a relative rate method are in good agreement. The 298 K preferred value is an average of the two values of Olariu et al. (2004). The assigned uncertainty reflects the fact that all of the data are from a single study.

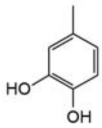
References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.
Olariu, R. I., Bejan, I., Barnes, I., Klotz, B., Becker, K. H. and Wirtz, K: Int. J. Chem. Kinet., 36, 577, 2004.

NO3_AROM9: 1,2-dihydroxy-4-methylbenzene

Last evaluated: November 2008; Last change in preferred values: November 2008

NO_3 +



→ **products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.60 \pm 0.06) \times 10^{-10}$	298 ± 2	Olariu et al., 2004	RR-FTIR (a)
$(1.35 \pm 0.04) \times 10^{-10}$	296 ± 2	Olariu et al., 2004	RR-FTIR (b)

Comments

(a) NO_3 radicals generated by the thermal decomposition of N_2O_5. Experiments were carried out in a 1080 L chamber at 1 bar of air. The concentrations of 1,2-dihydroxy-4-methylbenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-4-methylbenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxy-4-methylbenzene loss rate due to NO_3 radical reaction during the experiments. The measured rate coefficient ratio of $k(NO_3$ + 1,2-dihydroxy-4-methylbenzene)/$k(NO_3$ + 2,3-dimethyl-2-butene) = 2.80 ± 0.10 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

(b) NO_3 radicals generated by the thermal decomposition of N_2O_5. Experiments were carried out in the ~200 m^3 EUPHORE chamber at atmospheric pressure of air. The concentrations of 1,2-dihydroxy-4-methylbenzene and 2,3-dimethyl-2-butene (the reference compounds) were measured by FTIR spectroscopy. Wall losses of 1,2-dihydroxy-4-methylbenzene were measured and taken into account in the data analysis, and these contributed ~40% of the 1,2-dihydroxy-4-methylbenzene loss rate during the experiments. The measured rate coefficient ratio of $k(NO_3$ + 1,2-dihydroxy-4-methylbenzene)/$k(NO_3$ + 2,3-dimethyl-2-butene) = 2.36 ± 0.06 is placed on an absolute basis using $k(NO_3$ + 2,3-dimethyl-2-butene) = 5.72×10^{-11} cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.5×10^{-10}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The rate coefficients measured by Olariu et al. (2004) at 296-298 K in two reaction chambers differing in volume by a factor of ~200 using a relative rate method agree to within 20%. The 298 K preferred value is an average of the two values of Olariu et al. (2004). The assigned uncertainty reflects the fact that all of the data are from a single study.

References

Atkinson, R. and Arey, J.: Chem. Rev., 103, 4605, 2003.

Olariu, R. I., Bejan, I., Barnes, I., Klotz, B., Becker, K. H. and Wirtz, K: Int. J. Chem. Kinet., 36, 577, 2004.

Photolysis
VOCs (≥ C_4)

ID	Reactants		Products
P8	**butanone + h*v***	→	**products**
P23	**biacetyl + h*v***	→	**products**
P24	**i-butyraldehyde + h*v***	→	**products**
P26	***cis-/trans*-butene-2-dial + h*v***	→	**products**
P27	**4-oxopent-2-enal + h*v***	→	**products**
P28	**2-nitrophenol + h*v***	→	**products**
P30	**benzaldehyde + h*v***	→	**products**
P31	**3-methyl-2-nitrophenol + h*v***	→	**products**
P32	**4-methyl-2-nitrophenol + h*v***	→	**products**

P8: butanone

Last evaluated: February 2021; Last change in preferred values: February 2021

$CH_3C(O)C_2H_5 + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH^{o}_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)C_2H_5 + h\upsilon \rightarrow CH_3 + C_2H_5CO$	(1)	352.6	339
$\rightarrow C_2H_5 + CH_3CO$	(2)	349.4	342
$\rightarrow CH_3 + C_2H_5 + CO$	(3)	395.3	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202-355	Martinez et al., 1992	(a)
260-360	Hynes et al., 1992	(b)
240-350	Mu and Mellouki, 2000	(c)
335-375	Chen and Venables, 2011	(d)
200-335	Brewer et al., 2019	(e)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ			
0.34 (1000 mbar, 298 K)	275 - 380	Raber and Moortgat., 1987	(f)
0.89 (68 mbar, 298 K)			
0.27 (1000 mbar, 298 K)	308	Baeza-Romero et al., 2005	(g)
0.74 (100 mbar, 298 K)			
0.16 (1000 mbar, 298 K)	320		
0.62 (100 mbar, 298 K)			

Comments

(a) Double-beam spectrophotometric measurements of mixtures of butanone and argon at a resolution of 0.5 nm. The cross-sections are given as averages over 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) centered on the reported wavelengths. $\sigma_{max} = 5.77 \times 10^{-20}$ cm^2 molecule^{-1} at 278 nm.

(b) Diode array spectrometer combined with a D_2 lamp were used to measure the absorption cross sections at 2 nm resolution between 260 and 360 K. The butanone concentration was determined by monitoring absorption of the 253.7 nm Hg line.

(c) Diode array spectrometer measurements of pure butanone at a resolution of 0.04 nm. The cross-sections are given over 1 nm intervals. $\sigma_{max} = 5.65 \times 10^{-20}$ cm^2 molecule^{-1} at 278 nm.

(d) Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy (IBBCEAS) measurements at a resolution of 0.31 nm (at 365 nm) and 296 K. Butanone was introduced in a N_2 stream into the cavity and its concentration quantified from the cross section at 320 nm.

(e) Measurements of the absorption cross sections (1nm resolution, 242-335 K) using a D_2 lamp and a spectrometer/CCD detector set-up. The concentration of butanone in the absorption cell was calculated from the total pressure and the butanone/N_2 mixing ratio, which was determined manometrically.

(f) Butanone was photolyzed in synthetic air at several pressures in the range 68 mbar to 1 bar using a broad-band light source (275 nm to 380 nm). The quantum yield for photolysis of butanone was calculated by comparison of its loss-rates compared to Cl_2, which served as chemical actimometer. Numerical simulation of the products formed (monitored by FTIR) indicated that photolysis over the wavelength region studied occurs mainly (85 ± 5 %) via channel 2.

(g) Quantum yields (308 and 320 nm) for acyl (RCO) radical production from butanone photolysis as a function of temperature (213-295 K) and pressure were determined via observing (with LIF) the OH product as a tracer for the primary RCO radical. OH was formed in the reaction between RCO and O_2 and normalised to data obtained at 248 nm, where the RCO yield is independent of pressure and temperature. The single bond cleavage of butanone leading to $CH_3CO + C_2H_5$ (channel (2)) was suggested to be dominant.

Preferred Values

Absorption cross-sections

λ (nm)	$10^{20}\,\sigma$ at 296K	$10^{20}\,\sigma_0$	$10^{20}\,\sigma_1$	λ (nm)	$10^{20}\,\sigma$ at 296K	$10^{20}\,\sigma_0$	$10^{20}\,\sigma_1$
200	2.92	-	-	278	5.79	5.540	800.0
201	1.46	-	-	279	5.77	5.500	877.0
202	0.96	-	-	280	5.75	5.460	906.0
203	0.47	-	-	281	5.72	5.420	954.0
204	0.24	-	-	282	5.67	5.370	977.0
205	0.19	-	-	283	5.61	5.290	1030.0
206	0.17	-	-	284	5.52	5.190	1090.0
207	0.16	-	-	285	5.43	5.080	1160.0
208	0.16	-	-	286	5.33	4.960	1220.0
209	0.15	-	-	287	5.23	4.860	1240.0
210	0.15	-	-	288	5.14	4.760	1260.0
211	0.15	-	-	289	5.03	4.660	1250.0
212	0.16	-	-	290	4.91	4.540	1250.0
213	0.16	-	-	291	4.75	4.380	1290.0
214	0.17	-	-	292	4.58	4.180	1350.0
215	0.18	-	-	293	4.39	3.980	1390.0
216	0.18	-	-	294	4.21	3.780	1470.0
217	0.19	-	-	295	4.05	3.610	1500.0
218	0.20	-	-	296	3.90	3.470	1490.0
219	0.21	-	-	297	3.76	3.340	1420.0
220	0.23	-	-	298	3.61	3.220	1360.0
221	0.24	-	-	299	3.45	3.070	1330.0
222	0.26	-	-	300	3.27	2.900	1300.0
223	0.28	-	-	301	3.07	2.700	1290.0
224	0.30	-	-	302	2.86	2.490	1310.0
225	0.33	-	-	303	2.66	2.280	1320.0
226	0.36	-	-	304	2.48	2.100	1330.0
227	0.40	-	-	305	2.30	1.930	1310.0
228	0.43	-	-	306	2.15	1.780	1290.0
229	0.47	-	-	307	2.00	1.640	1250.0
230	0.52	0.520	-34.2	308	1.85	1.520	1160.0
231	0.57	0.570	-39.2	309	1.71	1.400	1090.0
232	0.62	0.624	-42.6	310	1.56	1.270	1030.0
233	0.68	0.683	-51.4	311	1.41	1.130	981.0
234	0.74	0.746	-57.2	312	1.26	0.998	933.0
235	0.81	0.817	-64.6	313	1.12	0.875	888.0
236	0.88	0.892	-70.3	314	1.00	0.762	849.0
237	0.96	0.973	-79.0	315	0.89	0.661	806.0
238	1.04	1.060	-74.0	316	0.78	0.572	758.0
239	1.13	1.150	-86.6	317	0.69	0.491	710.0
240	1.23	1.250	-97.6	318	0.60	0.420	658.0

241	1.33	1.360	-121.0	319	0.52	0.355	606.0
242	1.44	1.470	-121.0	320	0.45	0.298	550.0
243	1.56	1.580	-132.0	321	0.38	0.247	495.0
244	1.68	1.700	-121.0	322	0.32	0.202	444.0
245	1.80	1.820	-108.0	323	0.27	0.164	394.0
246	1.94	1.960	-119.0	324	0.23	0.133	346.0
247	2.08	2.100	-143.0	325	0.19	0.107	298.0
248	2.22	2.250	-142.0	326	0.15	0.086	255.0
249	2.36	2.390	-148.0	327	0.13	0.069	218.0
250	2.51	2.530	-118.0	328	0.10	0.055	186.0
251	2.66	2.680	-116.0	329	0.08	0.043	158.0
252	2.83	2.850	-129.0	330	0.07	0.035	129.0
253	3.00	3.010	-116.0	331	0.05	0.030	98.8
254	3.16	3.180	-145.0	332	0.04	0.023	82.8
255	3.32	3.340	-132.0	333	0.03	0.018	68.4
256	3.48	3.480	-90.3	334	0.03	0.014	55.8
257	3.64	3.630	-61.0	335	0.02	0.012	44.4
258	3.81	3.800	-37.2	336	0.014	-	-
259	3.98	3.970	-47.9	337	0.011	-	-
260	4.16	4.140	-35.0	338	0.008	-	-
261	4.32	4.300	-34.8	339	0.007	-	-
262	4.46	4.430	25.5	340	0.005	-	-
263	4.59	4.540	91.4	341	0.005	-	-
264	4.72	4.660	128.0	342	0.003	-	-
265	4.87	4.790	174.0	343	0.003	-	-
266	5.01	4.940	181.0	344	0.002	-	-
267	5.16	5.080	187.0	345	0.001	-	-
268	5.28	5.190	223.0	346	0.001	-	-
269	5.37	5.270	284.0	347	0	-	-
270	5.45	5.320	355.0	348	0.001	-	-
271	5.51	5.360	426.0	349	0	-	-
272	5.58	5.410	503.0	350	0	-	-
273	5.65	5.470	539.0	351	0	-	-
274	5.72	5.540	545.0	352	0.001	-	-
275	5.77	5.580	592.0	353	0	-	-
276	5.80	5.590	634.0	354	0	-	-
277	5.80	5.580	705.0	355	0	-	-

Units of σ are cm^2 $molecule^{-1}$

Quantum Yields

An expression for calculating wavelength, pressure and temperature dependent quantum yields is given below.

Quantum yields at 1 bar and 298 K are $\phi(280\ nm) = 0.65$, $\phi(290\ nm) = 0.51$, $\phi(300\ nm) = 0.37$, $\phi(310\ nm) = 0.25$, $\phi(320\ nm) = 0.16$. Product studies and the pressure dependence of the quantum yield indicate that photolysis proceeds predominantly via formation of $C_2H_5 + CH_3CO$ (channel 2) (Raber and Moortgat, 1987), Calvert and Pitts (1966), Baeza-Romero et al (2005).

Comments on Preferred Values

The room temperature cross-sections reported in the published studies listed above are in excellent agreement close to the band maximum at 278 nm. Unpublished data from Schneider and Moortgat (1987) (reported by Keller-Rudek at al., 2013) are also in good agreement. The preferred absorption cross-sections at 296 K are taken from the most recent data (200-335 nm) of Brewer et al. (2019) extended to 355 nm by the measurements of Martinez et al. (1992). Brewer et al. provide an expression to calculate cross-sections (230-335 nm) at different temperatures, $\sigma(\lambda,T)$ using a two-state model with the following expression, which was validated with their experimental data:

$$\sigma(\lambda,T) = X_0\sigma_0 + X_1\sigma_1$$

Where $X_0 = (1+\exp(-2474.696/T))^{-1}$, $X_1 = 1- X_0$ and T is the temperature in Kelvin. Wavelength dependent values of σ_0 and σ_1 are listed in the Table above along with the room temperature cross-sections.

As the quantum yields for butanone dissociation are wavelength dependent, the use of single wavelengths (Baeza-Romero et al., (2005) and broad-band light sources (Raber and Moortgat 1987) makes direct comparison between the experimental results difficult. However, the room temperature results are in reasonable agreement both in terms of the magnitude of the quantum yield and the effect of pressure.

The quantum yields reported by Baeza-Romero et al (2005) for photodissociation of butanone in He are pressure and temperature dependent. Assuming that the quenching of butanone is independent of bath-gas identity (as these authors found to be the case for acetone), they present the following expression to calculate quantum yields in air:

$$\phi = (1 + A_1[M] + A_2)^{-1}$$

Where

$A_1 = a_1\exp(-a_1'((10^7/\lambda) -30488))$

$A_2 = a_2\exp(-a_2'((10^7/\lambda) -a_2''))^2)$

Note that this expression deviates from the original one (Baezo-Romero et al., 2005), in which there were typographical errors ($-10^7/\lambda$ was written insead of $10^7/\lambda$ and a_1'' instead of a_2'' in the appendix (for butanone, MEK).

$a_1 = 2.53 \times 10^{-19} (T/295)^{-5.03}$

$a_1' = 5.5 \times 10^{-4} (T/295)^{-0.382}$

$a_2 = 0.103 (T/295)^{-12.4}$

$a_2' = 1.95 \times 10^{-9} (T/295)^{-19.46}$

$a_2'' = 30006 \quad (T/295)^{-0.064}$

where the wavelength (λ) is in nm.

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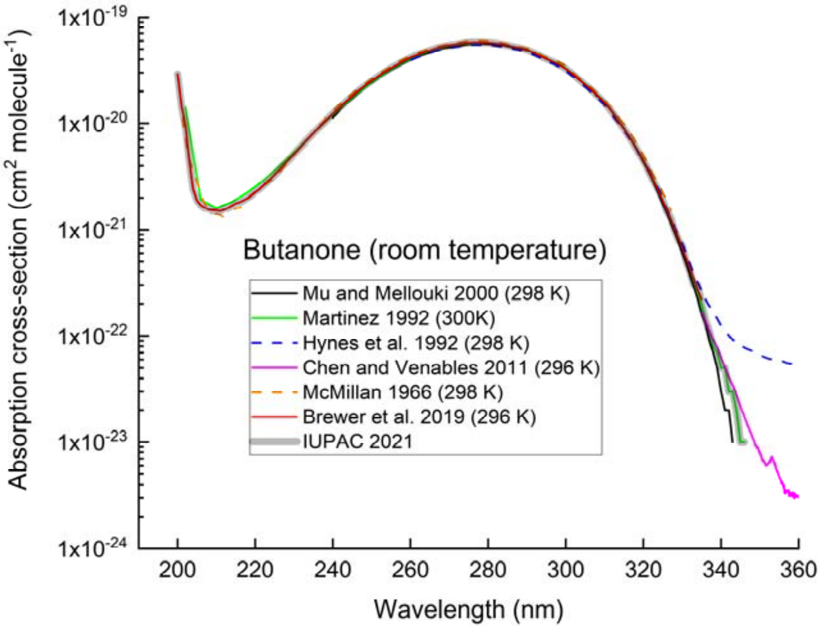
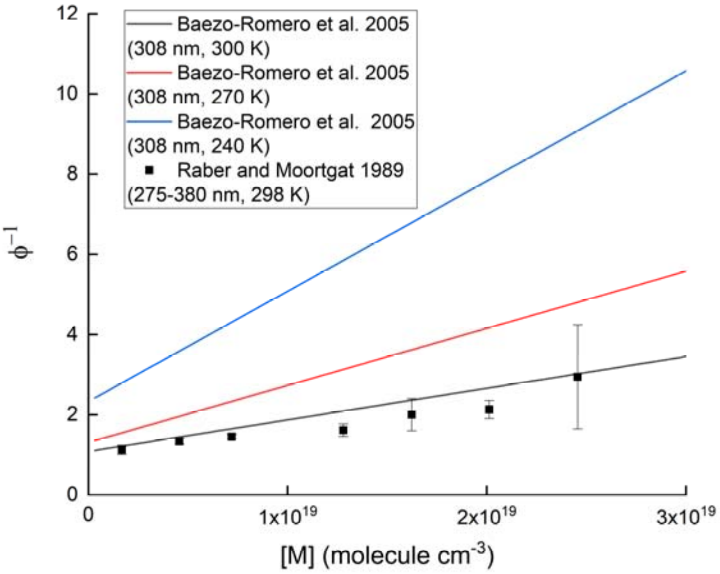


Absorption cross-sections for butanone at room temperature.



Pressure dependent quantum yields (in Stern-Volmer format) for photolysis of butanone at 308 nm and 275-380 nm. The lines (308 nm) were calculated using the expression of Baezo-Romero et al. (2005) given in the datasheet.

P23: biacetyl

Last evaluated: June 2011; Last change in preferred values: June 2011

$CH_3C(O)C(O)CH_3 + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction	ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$CH_3C(O)C(O)CH_3 \rightarrow CH_3C(O) + CH_3C(O)$ (1)		390
$\rightarrow CH_3C(O) + CH_3 + CO$ (2)		338
$\rightarrow 2CH_3 + 2CO$ (3)		300

Absorption cross-section data

Wavelength range/nm	Reference	Comments
208-476	McMillan, 1966	
230-470	Plum *et al.*, 1983	(a)
206-493	Horowitz *et al.*, 2001	(b)
184.9	Rajakumar *et al.*, 2008	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.16$	290-390	Plum *et al.*, 1983	(d)
$\phi(CH_3CO) = 0.76$(61 Torr) = 0.79(101 Torr) = 0.79(207 Torr) = 0.86(302 Torr) = 0.92(419 Torr) = 0.90(509 Torr) = 0.96(643 Torr)	248	Rajakumar *et al.*, 2008	(e)

Comments

(a) Spectrophotometric study (Cary 17-D) using biacetyl pressures of ~4 mbar to 17 mbar. Data taken from Spectral Atlas: (http://www.atmosphere.mpg.de/enid/2295) which gives absorption cross-sections read at 1- and 2-nm intervals from Fig. 1 of Plum et al (1983).

(b) Absorption measurements as a function of biacetyl pressure using a diode array spectrometer. Biacetyl pressure range of 0.5–10 Torr in which no deviations from Beer–Lambert law were observed. Cross-sections averaged over 1 nm intervals are listed. Reported accuracy of the biacetyl data in this work was ±4% or $\pm 1 \times 10^{-21}$ cm^2 molecule^{-1}, whichever was the larger.

(c) UV absorption measurements were made using a Hg pen-ray lamp light source at 184.9 nm combined with narrow bandpass filters and a photodiode detector. The cross-section determined for this wavelength was 1.46×10^{-18} cm^2 molecule^{-1}. The concentration of biacetyl was determined by UV absorption at 248 nm, using the cross-section of Horowitz et al. (2001).

(d) Rate of photolysis of biacetyl in air mixtures at atmospheric pressure measured in an environmental chamber. The quantum yield for the photodissociation of biacetyl was obtained by comparison of the measured rate of removal of glyoxal with the rate of photolysis of NO_2 under similar experimental conditions.

(e) Quantum yields determined from CH_3CO production measured in its visible absorption band (490 - 660 nm) by CRDS following photolysis of biacetyl at 248 nm in a crossed beam pulsed laser photolysis cell. CH_3CO yields were determined relative to those from a reference reaction; HO + CH_3CHO, with HO produced by co-photolysis of H_2O_2. Cited data for $\phi(CH_3CO)$ were for N_2 bath gas, a weaker pressure dependence was found for He.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
206	10.30	303	1.46	400	5.12
207	9.86	304	1.38	401	5.19
208	9.14	305	1.32	402	5.26
209	7.97	306	1.27	403	5.38
210	6.74	307	1.21	404	5.54
211	5.82	308	1.10	405	5.75
212	5.18	309	0.95	406	6.00
213	4.70	310	0.82	407	6.26
214	4.29	311	0.71	408	6.47
215	3.90	312	0.62	409	6.59
216	3.55	313	0.54	410	6.69
217	3.21	314	0.48	411	6.82
218	2.90	315	0.44	412	6.97
219	2.58	316	0.41	413	7.11
220	2.26	317	0.38	414	7.31
221	1.96	318	0.36	415	7.47
222	1.70	319	0.34	416	7.57
223	1.50	320	0.33	417	7.62
224	1.35	321	0.33	418	7.51
225	1.27	322	0.32	419	7.39
226	1.23	323	0.30	420	7.37
227	1.24	324	0.26	421	7.32
228	1.28	325	0.23	422	7.25
229	1.34	326	0.21	423	7.24
230	1.41	327	0.20	424	7.13
231	1.47	328	0.19	425	6.98
232	1.53	329	0.19	426	6.81
233	1.59	330	0.20	427	6.57
234	1.68	331	0.20	428	6.43
235	1.80	332	0.21	429	6.34
236	1.92	333	0.20	430	6.31
237	2.09	334	0.22	431	6.40
238	2.15	335	0.23	432	6.63
239	2.21	336	0.25	433	6.78
240	2.29	337	0.26	434	6.78
241	2.39	338	0.28	435	6.72

242	2.54	339	0.30	436	6.56
243	2.69	340	0.30	437	6.40
244	2.80	341	0.32	438	6.42
245	2.89	342	0.35	439	6.28
246	2.94	343	0.37	440	6.51
247	2.99	344	0.39	441	6.67
248	3.05	345	0.41	442	6.99
249	3.15	346	0.44	443	7.23
250	3.31	347	0.47	444	6.85
251	3.48	348	0.50	445	6.49
252	3.60	349	0.53	446	5.90
253	3.68	350	0.57	447	5.43
254	3.73	351	0.61	448	5.01
255	3.75	352	0.65	449	4.33
256	3.78	353	0.68	450	4.06
257	3.84	354	0.73	451	3.44
258	3.94	355	0.77	452	3.20
259	4.09	356	0.82	453	2.65
260	4.27	357	0.86	454	2.16
261	4.41	358	0.92	455	1.72
262	4.46	359	0.97	456	1.39
263	4.49	360	1.02	457	1.14
264	4.49	361	1.08	458	0.85
265	4.48	362	1.19	459	0.73
266	4.49	363	1.26	460	0.55
267	4.54	364	1.33	461	0.45
268	4.63	365	1.41	462	0.36
269	4.81	366	1.49	463	0.28
270	4.95	367	1.57	464	0.22
271	5.00	368	1.66	465	0.18
272	4.98	369	1.76	466	0.14
273	4.92	370	1.85	467	0.12
274	4.85	371	1.94	468	0.10
275	4.76	372	2.02	469	0.08
276	4.70	373	2.10	470	0.07
277	4.68	374	2.17	471	0.06
278	4.67	375	2.25	472	0.05
279	4.68	376	2.33	473	0.04
280	4.71	377	2.41	474	0.04
281	4.73	378	2.50	475	0.03
282	4.65	379	2.58	476	0.03
283	4.50	380	2.68	477	0.03
284	4.32	381	2.79	478	0.02
285	4.14	382	2.92	479	0.02
286	3.94	383	3.07	480	0.02
287	3.77	384	3.22	481	0.02
288	3.62	385	3.39	482	0.02
289	3.50	386	3.53	483	0.02
290	3.38	387	3.67	484	0.02
291	3.28	388	3.82	485	0.02
292	3.20	389	4.00	486	0.01
293	3.11	390	4.17	487	0.01
294	2.96	391	4.34	488	0.02

295	2.73	392	4.47	489	0.02
296	2.50	393	4.56	490	0.02
297	2.29	394	4.62	491	0.02
298	2.10	395	4.67	492	0.02
299	1.93	396	4.73	493	0.02
300	1.77	397	4.82		
301	1.64	398	4.92		
302	1.54	399	5.02		

Quantum Yields

At 248 nm: $\phi_1 + \phi_2 = 0.76$ for $p < 80$ mbar;
$\phi_1 = 2$; $\phi_2 = 0$ for $p \rightarrow \infty$;
290 – 380 nm: $\phi_1 + \phi_2 + \phi_3 = 0.16$ (average for atmospheric photolysis at surface).

Comments on Preferred Values

Biacetyl exhibits two distinct absorption regions relevant for atmospheric photolysis. The first region consists of a broad band between 340 – 480 nm, on which three distinct peaks are superimposed at 417.2, 433.0 and 442.8 nm. The second region shows a broad band with some structure with a maximum absorption near 272 nm. The preferred values for the absorption cross-sections are based on those determined by Horowitz et al. (2001), which are in satisfactory agreement with the earlier data of Plum et al. (1983) and McMillan et al., 1966 (e.g. $\sigma_{max} = 4.65 \times 10^{-20}$ cm^2 molecule^{-1} at 270 nm for the second band). The values given above are averaged over 1 nm and are taken from the compilation in http://www.atmosphere.mpg.de/enid/, which also contains data at other resolution. The overall accuracy for both bands is estimated at ±5%. The single wavelength determination of Rajakumar et al. (2008) at 184.9 nm is consistent with a third strong absorption band below 200 nm indicated by the data of Horowitz, (2001).

The recommended quantum yields for $\phi_1 + \phi_2$ are based on the data of Rajakumar *et al.* (2008), which are the only wavelength-resolved quantum yield data that have appeared. The observed pressure dependence of $\phi(CH_3CO)$ is due to dissociation of initially formed excited CH_3CO^* and is reproduced reasonably well, over the range of pressures covered in this study, by a Stern–Volmer relationship for the quenching of CH_3CO^*. This analysis using an assumed high pressure limiting yield of $\phi^{\infty}(CH_3CO) = 2$, gave a zero pressure quantum yield of $\phi^{0}(CH_3CO) = 0.76 \pm 0.05$. The authors estimate the overall uncertainty in experimental values of $\phi(CH_3CO)$ from biacetyl photolysis at 248 nm to be 15% at the 2σ (95% confidence) level.

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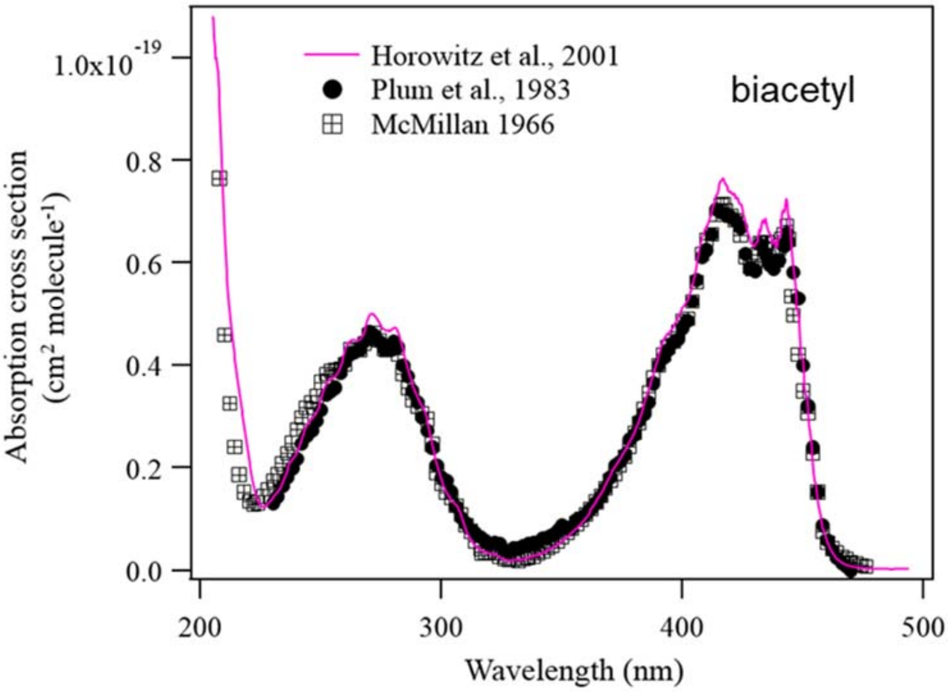

Absorption spectrum of biacetyl.

P24: *i*-butyraldehyde

Last evaluated: June 2010; Last change in preferred values: June 2010

i-$C_3H_7CHO + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
i-$C_3H_7CHO \rightarrow$ *i*-$C_3H_7 + HCO$	(1)		349
$\rightarrow C_3H_8 + CO$	(2)		
$\rightarrow$ *i*-$C_3H_7CO + H$	(3)		327
$\rightarrow CH_3 + CH_3CHCHO$	(4)		
$\rightarrow C_3H_6 + HCHO$	(5)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
265.2-334.0	Borkowski and Ausloos, 1962	(a)
206-444	McMillan, 1966	(b)
202-365	Martinez et al., 1992	(c)
280-330	Chen et al, 2002	(d)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi(HCO) = 0.20$	253.7	Desai et al, 1986	(e)
$\phi(HCO) = 0.45$	280.3		
$\phi(HCO) = 0.55$	302.2		
$\phi(HCO) = 0.88$	312.8		
$\phi(HCO) = 0.88$	326.1		
$\phi(HCO) = 0.69$	334.1		
$\phi^0(HCO) = 0.31 \pm 0.004$	280	Chen et al, 2002	(d)
$\phi^0(HCO) = 1.10 \pm 0.10$	320		
$\phi^0(HCO) = 0.94 \pm 0.06$	330		

Comments

(a) UV absorption measurements yielding molar extinction coefficients given in tabular form.

(b) Spectrophotometric study (Cary 17-D) using biacetyl pressures of ~4 mbar to 17 mbar. Cross-sections taken from Spectral Atlas (http://www.atmosphere.mpg.de/enid/2295) which gives absorption cross-sections read at 1- and 2-nm intervals from figure in Calvert and Pitts,1966.

(c) Cross-sections determined from absorption measurements as a function of i-C_3H_7CHO pressure using a diode array spectrometer, with a resolution of 0.25 nm.

(d) Photolysis of *n*-butyraldehyde and *i*-butyraldehyde at 5-nm intervals in the 280-330 nm region using dye laser photolysis combined with CRDS. Absorption cross-sections of *n*-butyraldehyde and *i*-butyraldehyde were obtained at each wavelength that was studied. The quantum yields of HCO and their dependences on photolysis wavelength, aldehyde pressure, and total pressure (10-525 mbar N_2) were determined from measurement of this photoproduct by CRDS, using a probe laser at 613 - 617 nm. The time dependence of [HCO] photofragment was analysed using a model of the post flash radical chemistry and Stern-Volmer self-quenching to determine the initial, zero pressure quantum yields, ϕ^0. Absolute absorption cross-section of HCO at the probe laser wavelength was determined using HCO from the formaldehyde photolysis reaction $H_2CO + h\nu \rightarrow HCO + H$, for which the HCO quantum yield is known, or from the $Cl + H_2CO \rightarrow HCl + HCO$ reaction. Quantum yields decreased with wavelength at both the longer and shorter end of the range. ϕ^0 between 280 – 330 nm was independent of N_2 pressure. At 285 nm, ϕ^0 was independent of p(i-C_3H_7CHO) (1.3-13 mbar range). At 325 nm (closer to the dissociation limit), ϕ(HCO) decreased with p(i-C_3H_7CHO), due to self quenching.

(e) Steady state photolysis of i-C_3H_7CHO was studied in the presence of O_2 at 263 and 294 K at several incident wavelengths. The quantum yields of CO and C_3H_6 were measured using GC. The primary quantum yields ϕ_1 (free radical channel) and ϕ_2 (molecular channel) were deduced from the difference in CO and C_3H_6 yields. The pulsed flash photolysis of *i*-C_3H_7CHO was also studied in the presence of air at 298 K. The transient UV absorption of peroxy radicals, formed by reaction of the photo-fragments with O_2, was monitored and relative quantum yields were obtained with 284.0, 302.5, 311.7, 325.0 and 330.5 nm incident radiation. The quantum yields were not pressure quenched, except at 330.5 nm, where a minimal pressure dependence was observed.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
202	0.93	273	4.05	321	2.280
206	0.40	274	4.14	322	2.175
208	0.28	275	4.35	323	2.076
210	0.23	276	4.69	324	1.951
212	0.20	277	4.91	325	1.842
214	0.17	278	4.81	326	1.710
216	0.15	279	5.03	327	1.584
218	0.12	287	5.73	328	1.397
220	0.12	288	5.79	329	1.195
222	0.09	289	5.85	330	0.950
224	0.11	290	5.87	331	0.785
226	0.09	291	5.84	332	0.672
228	0.12	292	5.84	333	0.567
230	0.12	293	5.88	334	0.490
232	0.16	294	5.92	335	0.425
234	0.18	295	5.94	336	0.357
236	0.24	296	5.86	337	0.297
238	0.27	297	5.78	338	0.257
240	0.34	298	5.73	339	0.215
242	0.41	299	5.69	340	0.173
244	0.51	300	5.59	341	0.147
246	0.61	301	5.48	342	0.123

248	0.77	302	5.43	343	0.081
250	0.91	303	5.36	344	0.059
252	1.11	304	5.29	345	0.034
254	1.27	305	5.15	346	0.025
256	1.51	306	4.98	347	0.019
258	1.71	307	4.73	348	0.015
260	1.96	308	4.57	349	0.013
261	2.11	309	4.41	350	0.011
262	2.13	310	4.27	351	0.010
263	2.43	311	4.13	352	0.009
264	2.60	312	3.99	353	0.008
265	2.79	313	3.86	354	0.005
266	2.88	314	3.73	355	0.004
267	3.16	315	3.61	356	0.003
268	3.33	316	3.48	357	0.001
269	3.45	317	3.26	358	0.001
270	3.49	318	2.82	359	0.001
271	3.75	319	2.60		
272	3.84	320	2.41		

Quantum Yields

λ/nm	ϕ_1
280	0.31 ± 0.04
285	0.50 ± 0.07
290	0.71 ± 0.04
295	0.91 ± 0.04
300	1.00 ± 0.14
305	0.92 ± 0.08
310	1.06 ± 0.07
315	1.06 ± 0.13
320	1.10 ± 0.10
325	1.10 ± 0.10
330	0.94 ± 0.06

Comments on Preferred Values

The absorption spectrum of i-butyraldehyde shows a single broad band between 230 and 350 nm, with a maximum at 294 nm. The cross-sections from earlier scanning UV spectrometer measurements of McMillan (1966) agree well with the diode array measurements of Martinez et al.(1992), although there are small differences in the details of the weak structure near the maximum and on the long wavelength side of the band. The less well λ-resolved measurements of Chen et al. (2002) suggest a systematic red-shift of the band compared to these data. The preferred absorption cross-sections are a simple average of the measurements of Martinez et al. (1992) and McMillan (1966) at each corresponding wavelength. The uncertainty on the cross-sections near the band centre are smaller than 4%.

The two studies cited reporting quantum yields both show wavelength dependence of the HCO radical channel, with ϕ(HCO) near unity around 310 nm, declining at both ends of the range 280 – 330 nm. The absolute values of the quantum yield of HCO at zero pressure measured directly by Chen et al. (2002) was generally slightly higher than the indirect determinations reported by Desai et al. (1986), but overall the agreement is good. Chen et al estimate and overall uncertainty of ~50%, comprising ±10% experimental error and 38%

systematic error arising mostly from the cross-sections for HCO (±20%) and i-C_3H_7CHO (10%; note that the σ values of Chen differ from the above IUPAC preferred values near the maximim). Both studies concluded that pressure quenching by N_2 or O_2 was negligible except near the photodissociation threshold, but efficient quenching of excited i-butyraldehyde by ground state i-butyraldehyde occurs at $\lambda < 310$ nm. The reduced ϕ(HCO) at $\lambda < 295$ nm is accounted for by the opening up of an additional photodissociation pathway (2) forming C_3H_8 + CO at higher photon energy. The Norrish Type II dissociation channel involving α-H transfer to give C_2H_4 + CH_2CHOH products is not available for i-butyraldehyde and it can be concluded that the overall quantum yield ϕ (= ϕ_1 + ϕ_2) = 1.0. The slight fall off in ϕ at the longest wavelengths near the photodissociation threshold could result from quenching by N_2

The preferred values of ϕ_1 are the direct measurements of Chen et al. for ϕ(HCO). For atmospheric photolysis of i-butyraldehyde the overall photolysis can be calculated with ϕ = 1.0, with the second contributing channel $\phi_2 = (1- \phi_1)$.

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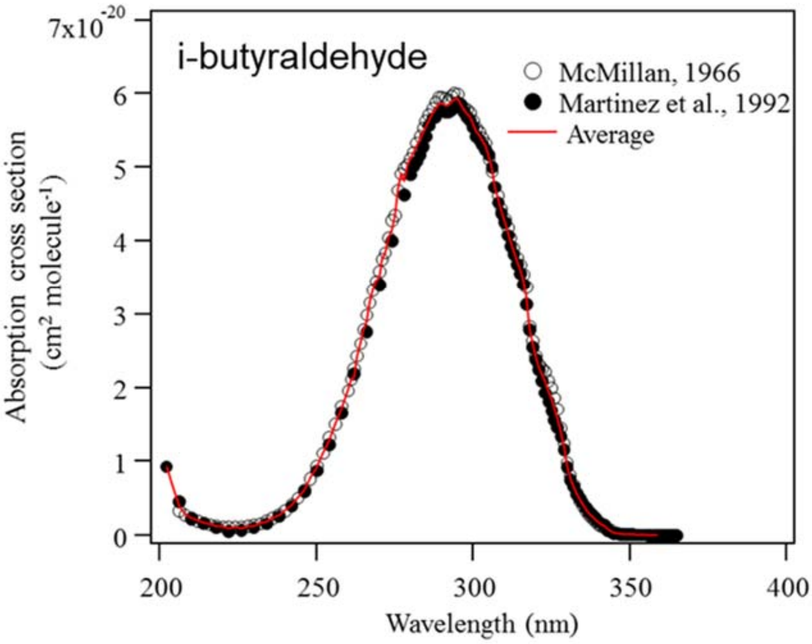

Absorption spectrum of *i*-butyraldehyde.

P26: butene-2-dial

Last evaluated: May 2012; Last change in preferred values: May 2012

cis-HC(O)CH=CHC(O)H + hυ → products
trans-HC(O)CH=CHC(O)H + hυ → products

Primary photochemical transitions

Reaction			$\lambda_{threshold}$/nm
HCOCH=CHCHO→ *trans/cis*		HCOCH=CHCHO *cis-/trans* (1)	
	→	HCOCH=CH + HCO (2)	~290
	→	HCOCH=CHCO + H (3)	
	→	2HCO + C_2H_2 (4)	~351
	→	$CH_3COCH=CH_2$ + CO (5)	<346
	→	3H-furan-2-one (6)	<346

Absorption cross-section data

Wavelength range/nm	Reference	Comments
193, 248, 308, 351	Tang and Zhu, 2005	(a)
220 - 460	Hufford et al., 1952	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5$)

Measurement	Wavelength range/nm	Reference	Comments
absolute quantum yields			
ϕ((HCO))= 0.55 ± 0.07	193	Tang and Zhu, 2005	(c)
ϕ((HCO)) = 0.12 ± 0.07	248		
relative quantum yields (φ %)			
$\varphi(1)$ = ~45 (*cis-/trans* & *trans-/cis*)	320 – 480	Bierbach et al., 1994	(d)
$\varphi(1)$ = ≤30 (*cis-/trans* & *trans-/cis*)	254		
$\varphi(2)$= ≥1.1	193	Tang and Zhu, 2005	(e)
$\varphi(2)$= ≥3.7	248		
$\varphi(2)$= ≥15	308		
$\varphi(2)$= ≥23	351		
$\varphi(6)$= 0	193		
$\varphi(6)$= ≥2.8	248		
$\varphi(6)$= ≥1.2	308		
$\varphi(6)$= ≥1.1	351		

Comments

(a) Cross-section data at 193 and 248 nm were determined by monitoring transmitted laser photolysis fluence as a function of butenendial pressure in the cell. The absolute cross-sections thus obtained were $(6.88 \pm 0.39) \times 10^{-18}$ and $(3.62 \pm 0.69) \times 10^{-19}$ cm^2 molecule^{-1} at 193 and 248 nm, respectively. The cited (1σ) error bars give estimated precision of the determination of the cross-sections. At 308 and 351 nm upper limits of $< 6 \times 10^{-21}$ cm^2 molecule^{-1} were given.

(b) UV absorption spectrum of purified (crystalline) fumaric dialdehyde dissolved in iso-octane was reported. The sample was mainly the *trans*- isomer. The spectrum showed two absorption bands, one peaked at 225 nm (ε =17 000 cm^{-1}) and the other peaked at 354 nm (ε = 70 cm^{-1}).

(c) Quantum yield of HCO production determined from CRDS measurement of HCO concentration at 613.80 nm., using an absorption cross-section of ~ 2.0×10^{-18} cm^2 molecule^{-1} at this wavelength. The system was calibrated at 248 nm relative to formaldehyde photolysis at this wavelength, for which the recommended ϕ((HCO))= 0.29; at 193 nm, HCO produced by the Cl + HCHO reaction, was used for calibration, with Cl produced by CCl_4 photolysis at this wavelength. Estimated overall uncertainty was 52% at 193 nm and 60% at 248 nm.

(d) Photo-oxidation studies in 1080 L quartz glass chamber surrounded by actinic fluorescent or low pressure mercury lamps. Total pressure 1000 mbar synthetic air and 296 ± 2 K. Loss of butene-2-dial (*cis*- & *trans*- isomers) and formation of products, were measured from time-dependence of FTIR absorption. The main products formed included maleic anhydride, HCHO, CH_3OH and CH_3OOH, with minor amounts of 3H-furan-2-one.

(e) Relative yields based on measurements, using FTIR, of end products (3H-furan-2-one and acrolein) of laser photolysis of butene-2-dial in a closed cell at 193, 248, 308 and 351 nm. The two products are assumed to result directly from channels (2) and (6). CO was observed at all wavelengths but could not be assigned to a specific channel due to complex secondary chemistry. Acetylene was also observed but only at 193 nm. If the *trans/cis* isomerisation yields of Bierbach et al. (1994) are included, the total photolysis yield of butene-2-dial is probably close to unity.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2	λ/nm	10^{20} σ/cm^2
193	688	310	1.40
200	732	320	1.92
210	758	330	2.29
220	841	340	2.38
225	966	350	2.06
230	933	360	1.57
235	395	370	1.34
240	149	380	1.07
248	36.2	390	0.73
250	17.3	400	0.45
260	0.80	410	0.26
265	0.22	420	0.13
270	0.07	430	0.05

272	0.04	440	0.03
280	0.27	450	0.02
290	0.54	460	0.01
300	1.00		

Quantum Yields

λ/nm	350-460	193	248	308	351
ϕ_1	0.45		<0.4		
ϕ_2	0	0.55± 0.29	0.12±0.07	0	0
ϕ_6		0	0.028	0.012	0.012

Comments on Preferred Values

There appear to be no measurements of the gas-phase UV/visible absorption spectrum of butene-2-dial but the absorption spectrum recorded by Hufford et al. (1952) in iso-octane solution resembles the gas phase spectrum of the related compound: 4-oxo-pentene-2-dial. The relative absorption coefficients extracted from Fig. 1 of this work were scaled to the absolute gas phase cross-section σ(248 nm) determined by Tang and Zhu (2005) to provide the recommended values of σ over the range 193 - 460 nm.

The only direct determination of primary quantum yields are those for HCO production reported by Tang and Zhu (2005). These results show that channel (2) only occurs at λ <308 nm and is a major channel at 193 nm. The relative yields of the photolysis co-products by Tang and Zhu (2005) are only lower limits, as secondary photolysis of these products occurs. Nevertheless it appears that channel (2) is not the only source of acrolein as it is observed at λ > 308 nm. 3H-furan-2-one was a minor product compared with acrolein. The *cis-/trans* isomerisation yields reported by Bierbach et al. (1994) are consistent with these results for channels (2) and (6), which are tentativly recommended. The major products observed from the photo-oxidation in synthetic air, reported by Bierbach et al. (1994), can be rationalised from secondary reactions of the primary photofragments.

References

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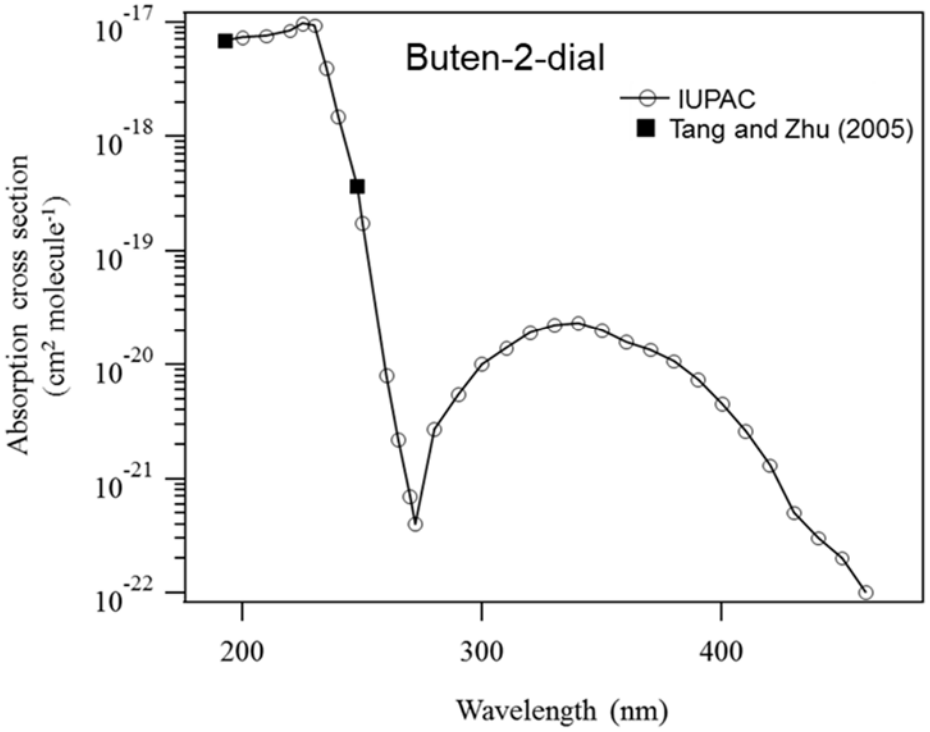

Absorption spectrum of butene-2-dial.

P27: 4-oxopent-2-enal

Last evaluated: May 2012; Last change in preferred values: May 2012

$CH_3C(O)CH=CHC(O)H + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction			ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
trans-/cis- $CH_3COCH=CHCHO$	→	*cis-/trans-* $CH_3COCH=CHCHO$ (1)		
	→	5-methyl-3*H*-furan-2-one (2)		
	→	$CH_3 + COCH=CHCHO$ (3)		~351
	→	$CH_3CO + CH=CHCHO$ (4)		<346
	→	$CH_3COCH=CH + HCO$ (5)		<346
	→	$CH_3COCH=CH_2 + CO$ (6)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
190-460	Xiang et al., 2007	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6$)

Measurement	Wavelength range/nm	Reference	Comments
absolute quantum yields			
ϕ((HCO))= 0.13±0.02 (*trans-*)	193	Xiang et al., 2007	(b)
ϕ((HCO))= 0.078±0.012 (*cis-*)			
ϕ((HCO)= 0.014±0.003(*trans-*)	248		(b)
ϕ((HCO))= 0.018±0.007(*cis-*)			
relative quantum yields (φ %)			
φ(1) = ~20-30 (*cis-/trans & trans-/cis*)	320 - 480	Bierbach et al., 1994	(c)
φ(1) = ≤20 (*cis-/trans & trans-/cis*)	254		
$\varphi(CH_3CO)$= 11±3	193	Xiang et al., 2007	(d)
$\varphi(CH_3CO)$= 17±9	248		
φ(2)= 1.2±0.1	193		
φ(2)= 2.1±1.5	248		
φ(2)= 5.3±1.3	308		
φ(2)= 5.5±1.7	351		
φ(3)= 25±8	193		
φ(3)= 33±10	248		
φ(3)= 31±12	308		
φ(3)= 23±9	351		

$\varphi(6)$= 25±10	193
$\varphi(6)$= 23±8	248
$\varphi(6)$= 40±10	308
$\varphi(6)$= 33±9	351

Comments

(a) Three techniques - conventional UV-Vis absorption spectrometry, laser fluence attenuation, and cavity ringdown spectroscopy were used to determine absorption cross-sections of purified samples of 4-oxopent-2-enal containing known amounts of *cis*- and *trans*- isomers defined by NMR. Cross-section data at 1 nm intervals in the 190-250 nm region were determined by absorption in a 10 cm cell placed in a UV/visible spectrometer, with variation of the 4-oxopent-2-enal pressure (mainly the *trans*- isomer) in the cell. The absolute uncertainty in these cross-section data is about 40-70%. Cross-section data at 193 and 248 nm were determined by monitoring transmitted laser photolysis fluence as a function of 4-oxopent-2-enal pressure in the cell. The absolute cross-section for 4-oxopent-2-enal with a *trans/cis* ratio of 0.082:1 was: 4.79×10^{-19} cm^2 $molecule^{-1}$ at 248 nm. The overall uncertainties in the determination of *cis*-4-oxopent-2-enal cross-sections were ±10% at 193 and 248 nm, and for *trans*-4-oxopent-2-enal were ±15% at 193 nm and ±25% at 248 nm. Cross-section data at 10 nm intervals in the 280-460 nm region were determined by cavity ring-down spectroscopy (CRDS). The method was calibrated using measurements of the cross-section for acetone at 298 K and 300 nm which was within 14% of the preferred value. Some differences were obtained in the CRDS absorbances of samples containing either mainly *cis*-isomer and containing mainly *trans*-isomer, especially at λ >400 nm. The relative amounts of *cis*- and *trans*-isomer in the mixtures was determined, which allowed the isomer-specific cross-sections for 4-oxopent-2-enal to be extracted.

(b) Quantum yield of HCO production determined from CRDS measurement of HCO concentration at 613.80 nm, using an absorption cross-section of $\sim 2.0 \times 10^{-18}$ cm^2 $molecule^{-1}$ at this wavelength, calibrated relative to formaldehyde photolysis at 248 nm, for which the recommended $\phi((HCO))$= 0.29.

(c) Photo-oxidation studies in 1080 L quartz glass chamber surrounded by actinic fluorescent or low pressure mercury lamps. Total pressure 1000 mbar synthetic air and 296 ± 2 K. Loss of 4-oxopent-2-enal (*cis*- & *trans*- isomers) and formation of products, from time-dependence of FTIR absorption. The main products formed included maleic anhydride, HCHO, CH_3OH and CH_3OOH, with minor amounts of 5-methyl-3H-furan-2-one.

(d) Relative yields based on measurements, using FTIR, of photolysis of 4-oxopent-2-enal and amounts of it's end products: 5-methyl-3H-furan-2-one, methyl vinyl ketone and ethane. The former two products are assumed to result directly from channels (2) and (6); ethane indicates CH_3 production in channel (3) or by dissociation of 'hot' CH_3CO in channel (4). Significantly increased CO yields were observed at 193 and 248 nm. If the *trans/cis* isomerisation yields of Bierbach et al. (1994) are included, the total photolysis yield of 4-oxopent-2-enal is close to unity, based on these results.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	10^{20} σ/cm^2 *cis-* isomer	10^{20} σ/cm^2 *trans-* isomer	10^{20} σ/cm^2 50/50 *cis/trans*
193	849	444	644
248	66.2	37.8	52
280	3.72	1.39	2.56
290	1.33	2.09	1.71
300	1.18	2.74	1.96
310	1.51	4.76	3.14
320	2.37	2.42	2.40
330	3.99	4.37	4.18
340	4.36	4.63	4.50
350	5.08	3.69	4.39
360	4.47	3.69	4.08
370	4.07	2.67	3.37
380	2.47	3.26	2.87
390	2.53	2.54	2.54
400	2.22	1.94	2.08
410	1.82	0.75	1.29
420	1.22	0.59	0.91
430	1.14	0.29	0.72
440	0.73	0.29	0.51
450	0.6	0.13	0.36
460	0.38	0.11	0.24

Quantum Yields

λ/nm	350-460	193	248	308	351
ϕ_1	0.3	-	<0.2	-	-
ϕ_2	0.05	0.01	0.02	0.05	0.05
ϕ_3	-	0.25	0.33	0.30	0.23
ϕ_4	0	0.11	0.17	-	-
ϕ_5	-	0.13	0.02	0	0
ϕ_6	0.33	0.25	0.25	0.40	0.33

Comments on Preferred Values

The cited data is the only reported quantitative study of the gas-phase UV/visible absorption spectrum of 4-oxopent-2-enal. It is composed of an absorption band in the shorter wavelength region (λ_{max} = 215 nm; $\pi \rightarrow \pi^*$ transition) and broad absorption bands in the longer wavelength region (λ_{max} = ~350 nm; most likely composed of two partially overlapping $n \rightarrow \pi^*$ transitions).

The absolute cross-sections for the wavelengths: 193 nm, 248 nm and 280 – 460 nm (10 nm intervals) are listed in the paper of Xiang et al. (2007), together with the cross-sections determined at 1 nm intervals by UV absorption on the 190 – 250 nm region for the mainly *trans*- isomer of 4-oxopent-2-enal. Results using the different methods in the different spectral regimes were in reasonable agreement. A detailed account of the uncertainties in the experimental data was also given.

The preferred cross-sections are the isomer specific values reported by Xiang et al. (2007), based on their measurements using CRDS and LAS. A simple average of these recommended values applies to a 50:50 mixture of *cis/trans* isomers, which corresponds approximately to an equilibrium mixture for ambient conditions.

The only direct determination of primary quantum yields are those for HCO production reported by Xiang et al. (2007), and these results show that this channel only occurs at $\lambda < 308$ nm and remains a minor channel even at 193 nm. However, the analysis of the relative yields of the photolysis products by Xiang et al. (2007), together with the *cis/trans* isomerisation yields reported by Bierbach et al. (1994), give a consistent picture of the photolysis channels in the absence of O_2; the preferred quantum yields are based on the assumption that the overall photolysis quantum yield of *cis* and *trans* 4-oxopent-2-enal is unity. The major products observed from the photo-oxidation in synthetic air, reported by Bierbach et al. (1994), can be rationalised from secondary reactions of the primary photofragments.

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Bierbach, A., Barnes, I., Becker, K. H. and Wiesen, E.: Environ. Sci. Technol., 28, 715, 1994.

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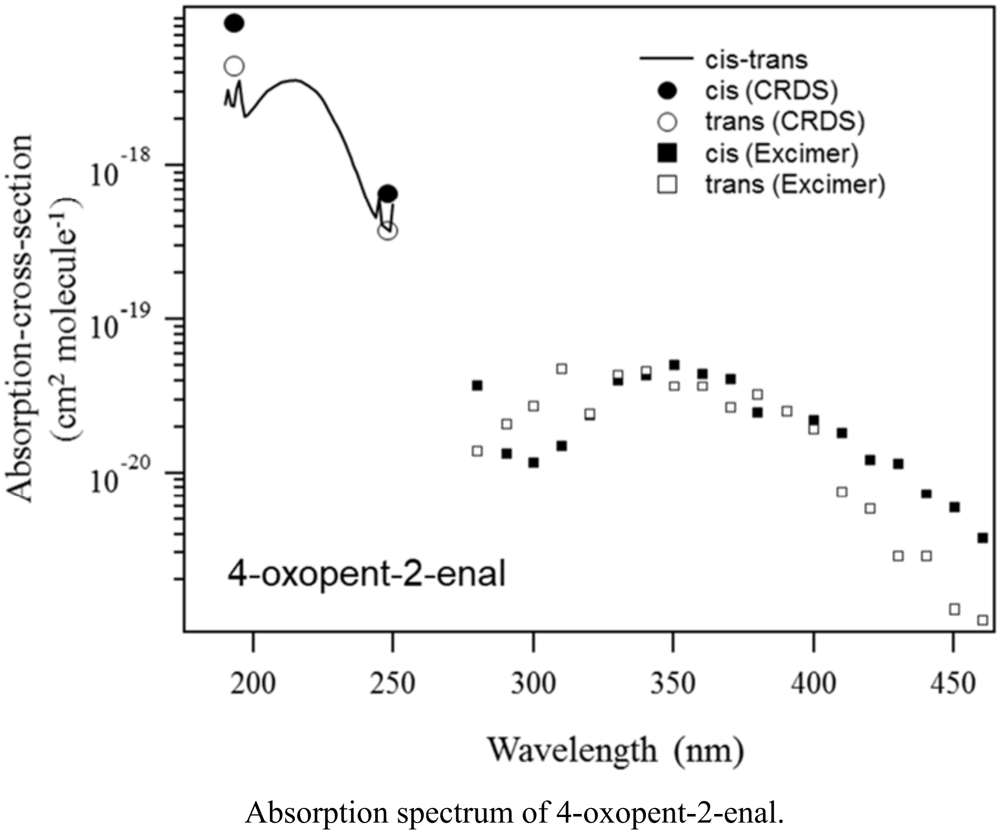

Absorption spectrum of 4-oxopent-2-enal.

P28: 2-nitrophenol

Last evaluated: February 2021; Last change in preferred values: February 2021

$C_6H_4(OH)NO_2 + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$C_6H_4(OH)NO_2 \rightarrow C_6H_4(OH) + NO_2$	(1)		
$C_6H_4(OH)NO_2 \rightarrow C_6H_4(O) + HONO$	(2)		
$C_6H_4(OH)NO_2 \rightarrow C_6H_4NO_2 + HO$	(3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
320 - 450	Chen et al., 2011	(a)
295 - 400	Sangwan and Zhu, 2016	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ (HONO) = 1.15×10^{-2}	320 – 480 (λ_{max} = 370)	Chen et al., 2011	(c)
ϕ (HONO) = 0.34 ± 0.09	308	Sangwan and Zhu, 2016	(d)
ϕ (HONO) = 0.39 ± 0.07	351		
ϕ (HO) = 0.69 ± 0.07	308		
ϕ (HO) = 0.70 ± 0.07	351		

Comments

(a) Absorption cross-sections of 2-nitrophenol were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source, giving a spectral range from 320 to 450 nm. The optical cavity was coupled into a 3.9 m^3 FEP chamber which contained the nitrophenols (99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross-sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% (1 s).

(b) Absorption cross sections were determined at 5 nm intervals in the region 295-400 nm using cavity ring-down spectroscopy. The probe beam over the 295−400 nm range was generated by frequency doubling the output of a dye laser pumped by the second harmonic of a Nd:YAG laser. 2-Nitrophenol sample (≥ 98% purity) was stored in a glass bulb connected to the cavity call. Cross section measurements were made under static conditons. Te experiments were conducted at 298 ± 2 °C.

(c) Chen et al. (2011) recalculated the quantum yield based on photolysis rates observed by Bardini (2006) under defined conditions in the EUPHORE chamber facility (Valencia, Spain), using their new gas phase cross-sections.

(d) Excimer laser photolysis of 2-nitrophenol at 308 and 351 nm with cavity ring-down spectroscopy. HONO and HO are direct products from 2-nitrophenol photolysis. Direct

NO_2 formation was not observed. The HO radical quantum yield was derived from the ratio of the HO concentration produced in the photolysis/probe laser overlap region to the absorbed photon density in the same region. The HONO quantum yields were determined by tuning the probe laser to HONO absorption peak at around 368.5 nm and measuring the cavity losses in the absence and presence of photolysis of 2-nitrophenol. The HO and HONO quantum yields were independent of nitrogen carrier gas pressure in the range 20−600 Torr.

Preferred Values

Absorption cross-sections

No recommendation

Quantum Yields

No recommendation

Comments on Preferred Values

Both the absorption spectrum shape and cross section values differ greatly (up to a factor of ~10) in the studies of Chen et al. (2011) and Sangwan and Zhu (2016), precluding firm recommendations. The discrepancy could be due to difficulties in handling 2-nitrophenol. However, both studies report that the absorption band of 2-nitrophenol peaks around 340 nm, which is blue-shifted by ~ 20 nm from the solution spectra recorded in acetonitrile (Bardini, 2006). The near-UV absorption of nitrophenols arises from the π(benzene ring) $\rightarrow$ π^*(nitro group) transition.

The value of ϕ(HONO) recalculated by Chen et al. (2011) from the measurements of Bardini (2006) in the EUPHORE chamber facility (Valencia, Spain), is substantially higher than earlier estimates e.g. by Bejan et al. (2006), which were based on absorbed light intensity calculated from the solution phase spectrum of 2-nitrophenol, which is red-shifted compared to the gas phase. The quantum yields are based on photolysis rates observed under defined conditions. Sangwan and Zhu (2016) have reported direct observation of both HONO and HO radicals at 308 and 351 nm and their quantum yield at these wavelengths. Further studies are required before recommendations can be made for both the quantum yields and absorption cross-sections.

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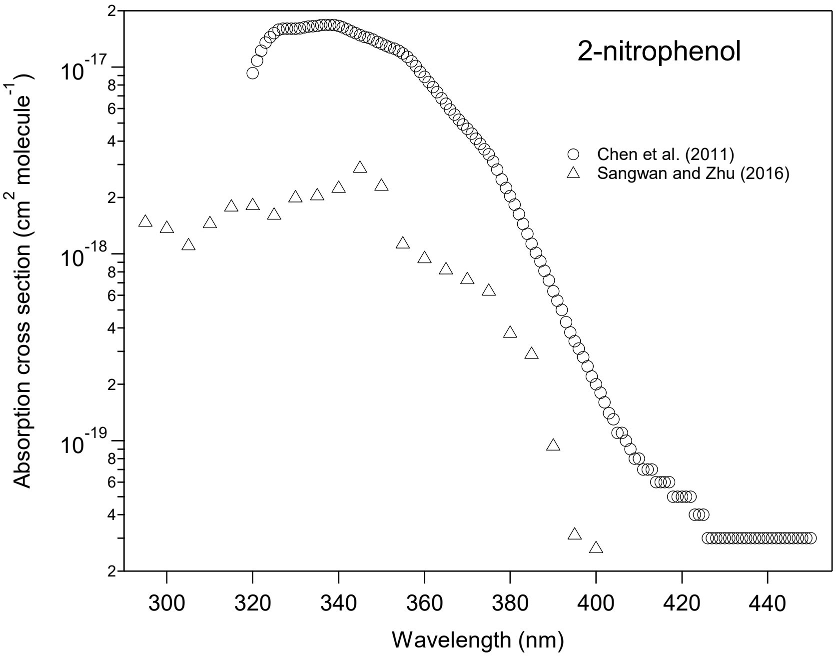

Absorption spectrum of 2-nitrophenol.

P30: benzaldehyde

Last evaluated: June 2012; Last change in preferred values: June 2012

$C_6H_5C(O)H + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction		ΔH°_{298}/kJ·mol^{-1}	$\lambda_{threshold}$/nm
$C_6H_5C(O)H \rightarrow C_6H_5 + HC(O)$	(1)	408.6	292
$C_6H_5C(O)H \rightarrow C_6H_5CO + H$	(2)	363.9	328
$C_6H_5C(O)H \rightarrow C_6H_6 + CO$	(3)	9.1	13.1 (μm)

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220 - 300	Nozière et al., 1994	(a)
245 - 300	Caralp et al., 1999	(b)
255 - 296	Etzkorn et al., 1999	(c)
280 - 308	Zhu and Cronin, 2000	(d)
252 - 368	Thiault et al., 2004	(e)
220 - 280	El Dib et al., 2006	(f)
280 - 400	Xiang et al., 2009	(g)
320 - 450	Chen et al., 2011	(h)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ_1(HCO) = 0.32±0.05	280	Zhu and Cronin, 2000	(d)
ϕ_1 (HCO) = 0.45±0.05	285		
ϕ_1 (HCO) = 0.29±0.05	308		

Comments

(a) The absorption cross-sections were determined by flowing nitrogen containing a calibrated concentration of benzaldehyde through a 70 cm reaction cell. UV light from a D_2 lamp passed twice through the cell into a monochromator/photomultiplier unit for conventional absorption measurements. Resolution not given.

(b) Same set up as (a); no experimental details given.

(c) UV absorption cross-sections were determined using a 1080 l quartz cell with a 0.5 m Czerny-Turner spectrometer coupled with a photodiode array detector (spectral resolution 0.15 nm). The maximum absolute absorption cross-section for benzaldehyde at the 284.1 nm peak was $\sigma = (4.40 \pm 1.82) \times 10^{-18}$) cm^2 molecule^{-1}.

(d) The UV photodissociation of benzaldehyde was investigated at wavelengths of 280, 285 and 308 nm by employing excimer or dye laser photolysis in combination with CRDS. Absorption cross-sections of benzaldehyde were obtained from attenuation of the photolysis light. The HCO radical photofragmentation product was detected by CRDS at

614 nm and amounts formed after 10 μs were determined using the absorption cross-section of HCO at the probe laser wavelength, determined relative to the photolysis reaction: $H_2CO + h\nu \rightarrow HCO + H$, for which the HCO quantum yield is known. The uncertainty on the quantum yields reflects experimental scatter.

(e) Absorption cross-sections for benzaldehyde were measured in the wavelength region 252–368 nm using two different systems (D_2 lamp-diode array and D_2 lamp-monochromator). In addition, cross-sections at 253.7 ($(8.5 \pm 1.3) \times 10^{-19}$ cm^2 molecule^{-1}), 312.2 ($(6.6 \pm 0.1) \times 10^{-20}$ cm^2 molecule^{-1}) and 365 nm ($(2.2 \pm 0.4) \times 10^{-20}$ cm^2 molecule^{-1}) were measured using a Hg pen ray lamp and were found in good agreement with those obtained using the D_2 lamp-diode array system. The absorption spectra of aromatic aldehydes have been found to exhibit fine structures similarly to aromatic hydrocarbons.

(f) Photolysis of a slow flowing mixture of Cl_2, N_2, O_2, and $C_6H_5CH_3$. Absorption cross-sections were determined by the "factor analysis method", where the spectrum obtained is refined and the concentrations of the main absorbing species in a complex mixture are extracted.

(g) Absorption measurements by CRDS. Cross-sections and error limits (standard deviations in the precision of the measurements) given at 5 nm intervals in the range.

(h) Absorption cross-sections of benzaldehyde were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source in the spectral range 320 - 450 nm. The optical cavity was coupled into a 3.9 m^3 FEP chamber which contained the benzaldehyde (>99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross-sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% (1σ).

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma$/cm^2	λ/nm	$10^{20}\sigma$/cm^2
220	21.000	310	0.0480
225	32.000	315	0.0658
230	39.000	320	0.0576
235	32.000	325	0.0649
240	24.000	330	0.0667
245	2.080	335	0.0677
250	1.300	340	0.0627
255	0.920	345	0.0471
260	1.300	350	0.0508
265	1.640	355	0.0385
270	1.990	360	0.0468
275	2.270	365	0.0418
280	1.720	370	0.0130
285	1.830	375	0.0043
290	0.120	380	0.0007
295	0.053	385	0.0002
300	0.043	390	0.0001
305	0.056	395	0.0002

Quantum Yields

Wavelength /nm	ϕ_1(HCO)
308	0.29±0.05

Comments on Preferred Values

The absorption spectrum of benzaldehyde consists of three distinct regions; an intense band between 200 - 250 nm (σ_{max} = 3.9 × 10^{-17} cm^2 $molecule^{-1}$ at 230 nm); a second band between approx. 250 - 290 nm (σ_{max} = 3.9 × 10^{-17} cm^2 $molecule^{-1}$ at 230 nm); and a weaker absorbing plateau region with superimposed structure between 300 - 370 nm. The cross-section data of most of the studies are in reasonable agreement except for those of Noziere et al. (1999) which are systematically higher, and those of Zhu and Cronin (2000), which are significantly lower than other measurements, except at 318 nm where they are slightly higher. Part of the differences arise from different resolution of the measurements using narrow band (laser) and broad-band techniques, especially in regions with discrete absorption features. The most recent CEAS measurements of Chen at al. (2011) confirm the detailed structure in the near UV observed by Thiault et al. (2004), but the authors note a blue-shift in the wavelength calibration in the Thiault et al. results at λ >335 nm, and an offset in their absorption at λ > 380 nm, probably resulting from a baseline shift or noise.

The preferred absorption cross-sections at λ > 295 nm are averaged values from the measurements of Thiault et al.(2004) blue shifted by 4 nm between 335 and 375 nm, Xiang et al. (2009) and Chen et al. (2011) in the regions of data overlap. Between 255 nm < λ < 295 nm the preferred values are average values of the data from Etzkorn et al. (1999), Thiault et al. (2004), and El Dib et al. (2006). The data of El Dib et al. (2006) are recommended for λ < 255 nm.

The recommended quantum yield ϕ(HCO) at 308 nm is the wavelength resolved value reported by Zhu and Cronin (2000). This gives a lower limit to the overall ϕ. The values at shorter wavelength may be unrepresentative due to fine structure effects in this structured part of the spectrum. Nevertheless, these results indicate that photolysis is a potentially important removal process for aromatic aldehydes in the troposphere.

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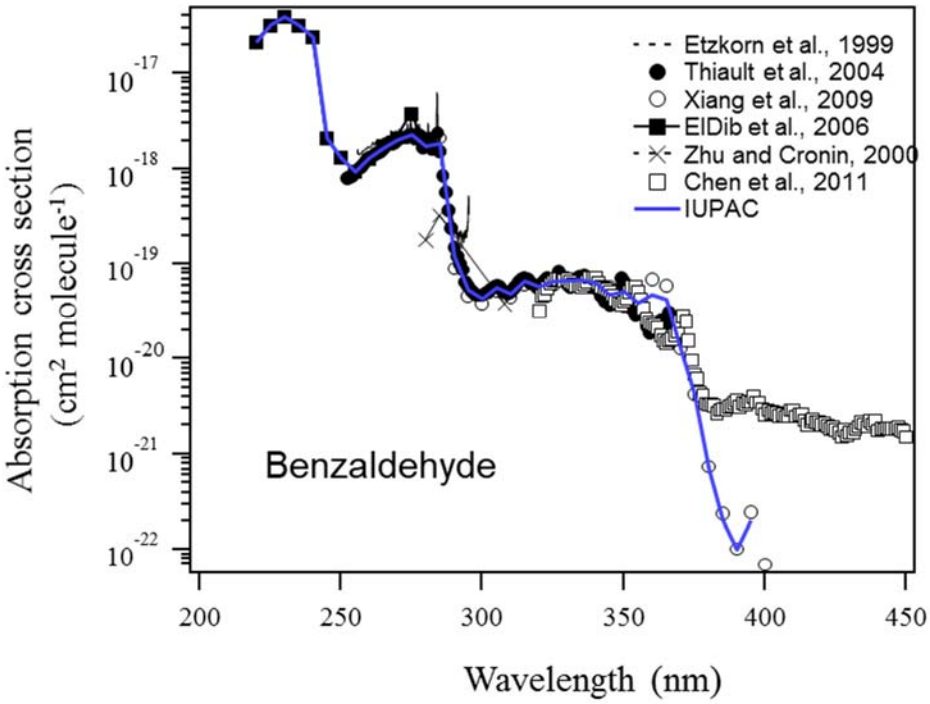

Absorption spectrum of benzaldehyde.

P31: 3-methyl-2-nitrophenol

Last evaluated: February 2021; Last change in preferred values: February 2021

$CH_3C_6H_3(OH)NO_2 + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction	
$CH_3C_6H_3(OH)NO_2 \rightarrow CH_3C_6H_3(OH) + NO_2$	(1)
$CH_3C_6H_3(OH)NO_2 \rightarrow CH_3C_6H_3(O) + HONO$	(2)

Absorption cross-section data

Wavelength range/nm	Reference	Comments
320 – 450	Chen et al., 2011	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ(HONO) = 1.5×10^{-4}	320 – 480 (λ_{max} = 370)	Bejan et al., 2006	(b)

Comments

(a) Absorption cross-sections of 3-methyl-2-nitrophenol were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source, giving a spectral range from 320 to 450 nm. The optical cavity was coupled into a 3.9 m^3 FEP chamber which contained the nitrophenols (99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross-sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% (1σ).

(b) The photolysis of nitrophenols was studied in a glass flow reactor, irradiated by fluorescent lamps emitting 300-500 nm. Concentration of 3-methyl-2-nitrophenol measured by FTIR and of the HONO product by derivativisation on-line followed by LPAS. Value of ϕ(HONO) was estimated from photolysis rate and absorbed intensity calculated from the solution phase spectrum of 3-methyl-2-nitrophenol.

Preferred Values

Absorption cross-sections

No recommendation

Quantum Yields

No recommendation

Comments on Preferred Values

The cross sections for 3-methyl-2-nitrophenol reported by Chen et al. (2011) appear to be the only gas-phase spectra of this compound in the literature, although solution spectra of the nitrophenols have been measured. The absorption of 3-methyl-2-nitrophenol was observed to vary linearly with concentration and the resulting spectrum is shown below. Similarly to 2-nitrophenol (see data sheet P28), the absorption band of 3-methyl-2-nitrophenol peaks around 340 nm, which is blue-shifted by ~ 20 nm from the solution spectra recorded in acetonitrile (Bardini 2006). The near-UV absorption of nitrophenols arises from the π(benzene ring) → π*(nitro group) transition. In view of the large disagreement between the gas-phase absorption spectra reported for 2-nitrophenol by Chen et al. (2011) and Sangwan and Zhu (2016) (see data sheet P28), we currently make no recommendation for the absorption cross sections of 3-methyl-2-nitrophenol.

Bejan et al. (2006) showed that HONO was a direct product of photolysis. However, the value of ϕ(HONO) reported by Bejan et al (2007) is likely to be underestimated since it was based on absorbed light intensity calculated from the solution phase spectrum of 3-methyl-2-nitrophenol, which Chen et al. (2011) show is redshifted compared to the gas phase. Further studies are required before recommendations can be made for both the quantum yields and absorption cross-sections.

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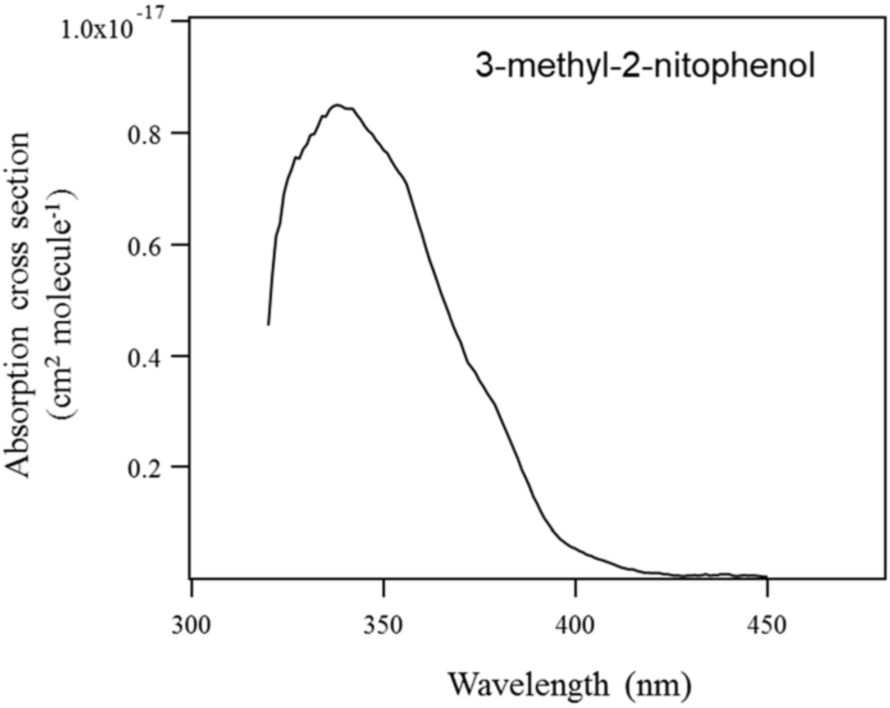

Absorption spectrum of 3-methyl-2-nitrophenol.

P32: 4-methyl-2-nitrophenol

Last evaluated: February 2021; Last change in preferred values: February 2021

$CH_3C_6H_3(OH)NO_2 + h\upsilon \rightarrow$ products

Primary photochemical transitions

Reaction	
$CH_3C_6H_3(OH)NO_2 \rightarrow CH_3C_6H_3(OH) + NO_2$	(1)
$CH_3C_6H_3(OH)NO_2 \rightarrow CH_3C_6H_3(O) + HONO$	(2)

Absorption cross-section data

Wavelength range/nm	Reference	Comments
320 – 450	Chen et al., 2011	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ (HONO) = $\sim 10^{-4}$	320 – 480 (λ_{max} = 370)	Bejan et al., 2006	(b)

Comments

(a) Absorption cross-sections of 4-methyl-2-nitrophenol were measured using incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) with a Xe arc light source, giving a spectral range from 320 to 450 nm. The optical cavity was coupled into a 3.9 m^3 FEP chamber which contained the nitrophenols (99% purity) diluted to < 100 ppbv in purified air. The optical system was calibrated using methyl vinyl ketone absorption at 360 nm. Cross-sections given at 1 nm intervals; overall error limits were estimated from standard deviations in the precision of the measurements, and other sources, to be 14% (1 σ).

(b) The photolysis of nitrophenols was studied in a glass flow reactor, irradiated by fluorescent lamps emitting 300-500 nm. Concentration of 4-methyl-2-nitrophenol measured by FTIR and of the HONO product by derivativisation on-line followed by LPAS. HONO formed but ϕ(HONO) was not determined.

Preferred Values

Absorption cross-sections

No recommendation

Quantum Yields

No recommendation

Comments on Preferred Values

The cross sections for 4-methyl-2-nitrophenol reported by Chen et al. (2011) appear to be the only gas-phase spectra of this compound in the literature, although solution spectra of the nitrophenols have been measured. The absorption of 4-methy-2-nitrophenol was observed to vary linearly with concentration and the resulting spectrum is shown below. The absorption band of 4-methy-2-nitrophenol peaks around 340-350 nm, which is blue-shifted by ~30 nm from the solution spectra recorded in acetonitrile (Bardini, 2006). The near-UV absorption of nitrophenols arises from the π(benzene ring) → π*(nitro group) transition. In view of the large disagreement between the gas-phase absorption spectra reported for 2-nitrophenol by Chen et al. (2011) and Sangwan and Zhu (2016) (see data sheet P28), we currently make no recommendation for the absorption cross sections of 4-methyl-2-nitrophenol.

The photolysis frequency reported by Bejan et al. (2007) was approximately a factor of 2 slower than for 3-methyl-2-nitrophenol. Values of ϕ(HONO) were not given. Further studies are required before recommendations can be made for both the quantum yields and absorption cross-sections.

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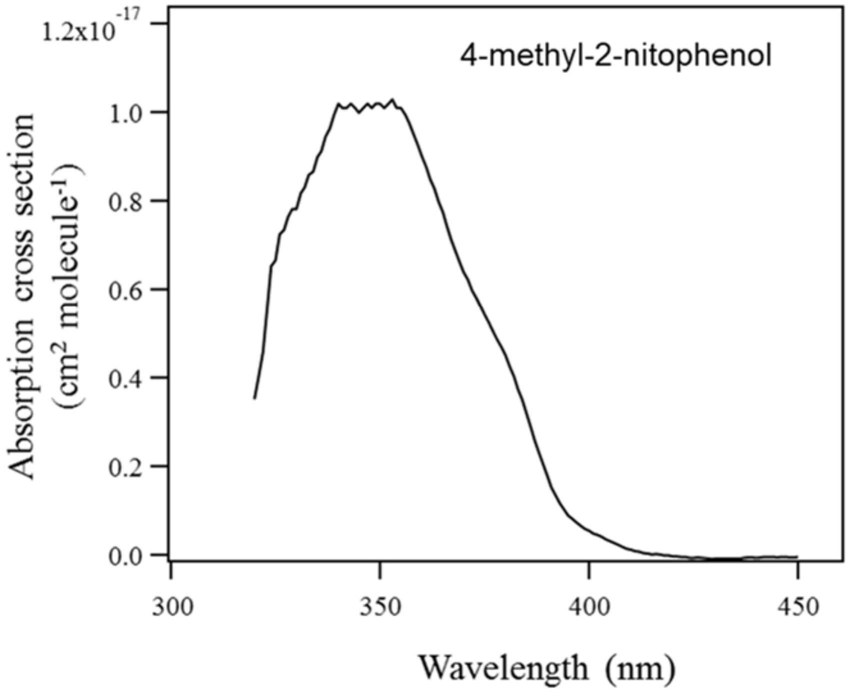

Absorption spectrum of 4-methyl-2-nitrophenol.